THE DILUTE ACID HYDROLYSIS OF TASMANIAN WOODS IN A PERCOLATION APPARATUS.

by

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PREFACE.

Investigations in the field of wood hydrolysis at the University of Tasmania were planned in a general way by Professor E. E. Kurth in 1940-41 and laboratory work was commenced in 1942 by B. J. Ralph B.Sc. and A.B. Wardrop M.Sc. They published a paper on the dilute acid autoclaving of e.obliqua in the April 1946 Edition of the Journal of the Australian Chemical Institute.

The investigations carried out since February 1944 are described in this paper. In 1944 M.H.R. Shipp B.Sc. and D. H. Foster B.Sc. continued the work on wood hydrolysis under the direction of Mr. B. J. Ralph. Whereas previous experiments had been confined to an autoclave the hydrolytic process was now carried out in a percolator in which dilute acid was passed continuously through the wood. They made a preliminary investigation on the effect of the variables of temperature and time on the hydrolysis of a sample of e.obliqua.

In 1945 Shipp and O. G. Ingles B.Sc. modified the percolator, and under the direction of Mr. B. J. Ralph they performed experimental work on the investigation of the effect of temperature, strength of acid , time and rate of acid flow on the hydrolysis of e.obliqua. These results were interpreted by Foster and are presented in this paper.

Foster returned to the work on wood hydrolysis in February 1946 after an absence of twelve months in the R.A.A.F. He investigated the hydrolysis of eleven different Tasmanian woods under the direction of Prof. E. E. Kurth and carried out some work on the analysis of specific sugars and organic acids

in sugar solutions obtained by hydrolysing wood.

The author wishes to express his thanks to Professor E. E. Kurth and Mr. B. J. Ralph for their every assistance and their valuable advice.

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(D. H. Foster)

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C O N T E N T S.

AN INVESTIGATION OF THE ACID HYDROLYSIS OF TASMANIAN WOODS BY MEANS OF A PERCOLATION APPARATUS.

Introduction.

From the point of view of wood hydrolysis the constituents of wood fall into three main groups.

(1) Lignin which is relatively unattacked.

(2) Extractives such as tannins, kinos, fats, waxes, essential oils and mineral constituents, a large portion of which are dissolved in the hot acid.

(3) The carbohydrate portion which is hydrolysed to its constituent units viz: Hexose and pentose sugars, and small amounts of uronic acids, acetic acid and methyl alcohol.
This paper is mainly concerned with this portion of the wood.

The total carbohydrate portion of the wood (holocellulose) is composed of orthoglucosan or true cellulose and hemicelluloses. The true cellulose is not easily hydrolysed by dilute acids excepting at temperatures of about 180°C. It possesses micellar structure, which means that it contains submicroscopic crystalline supermolecular units called micells (1). According to the Frey Wyssling theory the true cellulose is partly crystalline and partly amorphous, but the amount of crystalline material does not yet seem to have been determined.

According to Wise [2] hemicellulose consists of cellulosan and polyuronide hemicellulose. The cellulosan consists largely of xylan in hardwoods and of xylan and mannan in softwoods[3]. It is closely associated with the true cellulose but is generally of shorter chain length. The polyuronide hemicelluloses are cell wall encrusting substances consisting mainly of hexose, pentose and uronic acid structual units. They are thought to be amorphous and of short chain length compared with true cellulose.

Wise (4) states that it is not possible to consider wood cellulose (i.e. true cellulose and cellulosan) as being a simple mixture of long chain cellulosic material typified by cotton cellulose, mixed with a certain amount of short chain cellulosan. Any separation that is effected is arbitrary and depends on choice of reagents and time and temperature of treatment.

Recently Mitchell (5) separated the cellulosic constituents of western hemlock as soluble nitrates with very little degradation of the original material. The isolated nitrates were fractionated with solvents and the degree of polymerisation of the fractions was estimated by viscosity measurements. He showed that there are <u>two</u> distinct groups of cellulosic material in wood - namely hemicellulose which has an average degree of polymerisation (D P) of about 70 and which amounts to 30% of the total and true cellulose which has an average D P of 2,000 - 2,500 and represents the remaining 70% of cellulose in the wood.

This corresponds to a wood analysis of about 50% true cellulose, 20% hemicellulose and 30% lignin on solvent extracted moisture free western hemlock. Mitchell includes both the cellulosan and the polyuronide hemicellulose of Norman in what he calls hemicellulose. Further evidence for Mitchell's point of view will be given in this paper.

The advantages of percolation over autoclaving methods of dilute acid hydrolysis depend on the fact that cellulose is only slowly hydrolysed while the simple sugars are relatively easily decomposed. In percolation methods the sugars can be rapidly removed after they are formed, the speed of removal depending on the rate of flow of the dilute acid.

The first percolation process was that of Scholler (6) which was based on an investigation of the kinetics of hydrolysis of cellulose dextrin by Luers (7). As originally developed, the Scholler process was one in which acid was continuously passed through the cellulose material but various modifications were introduced (8) such as rest periods steaming and introduction of acid in batches. The value of these modifications has not been proven and in none of the literature listed has there been disclosed a systematic investigation of the variables of time, temperature, rate of acid flow and strength of acid.

A percolation pilot plant has been built at Madison, Wisconsin (10). Its capacity is 400 lbs. of dry wood substance and it has been devoted to the production of simple sugars for fermentation.

At first the wood was hydrolysed by passing successive batches of dilute sulphuric acid through the wood but more recently (11) the process has been modified. In the process now used .5 - .6% sulphuric acid is passed continuously through the wood for about three hours commencing at 150° c. and rising to 180° c. Australian woods have been hydrolysed in this apparatus (12).

Luers (7) was the first to study the kinetics of hydrolysis with dilute acid. He hydrolysed cellulose dextrin with dilute sulphuric acid and found that the hydrolysis of the cellulose dextrin and the decomposition of the simple sugars were both reactions of the first order.

More recently Saeman (9) studied the hydrolysis of wood and the decomposition of simple sugars by dilute acid in sealed glass bombs. He presented data to clarify the reactions occurring in wood sacchorification. Hydrolysis of hemicellulose occurred easily and required an insignificant time in comparison with that required for hydrolysis of the resistant portion of the cellulose. The decomposition of the sugar and the hydrolysis of the resistant portion of the cellulose were both first order reactions and possessed rates of similar magnitude. He showed that the efficiency of conversion of cellulose to reducing sugars increased with increasing temperature and increasing acid concentrations. He made these conclusions from a consideration of the amount of cellulose left in the glass bomb after hydrolysis.

The process here described is a percolation process in which dilute sulphuric acid is passed continuously through the wood. The effect of the variables of time, temperature, acid concentration and rate of acid flow have been investigated. Decomposition of simple sugars is small and the amount decomposed in any given time is a constant proportion of the amount of sugar produced in that time. Hence, from a consideration of sugar produced after a series of time intervals it is possible to calculate the first order reaction constant for the hydrolysis of the "more resistant cellulose" of the wood under any given set of conditions. This method has been applied to e.obliqua under the varying conditions specified above and to eleven other Tasmanian woods under a standard set of conditions.

Preparation of Woods for Hydrolysis.

All logs were supplied and certified to be true specimens by the Tasmanian Government Forestry Department. The logs were split into radial sections and reduced to shavings or sawdust a few days after they were cut in the forest.

In Section A of this work, wood shavings were used. The log was split into radial sections and one of these was almost entirely converted into shavings of about .02" thickness. The shavings were set out to dry in a large room and were thoroughly mixed about every two days until the moisture content was about 12%.

For Sections B and C, radial sections of logs were sawed transversely with a circular saw until sufficient sawdust was obtained. It was then dried in the same manner as were the shavings.

Finally the sawdust was sieved through a 14 mesh B S S sieve and all the -14 fraction was used in the percolation treatment.

These methods ensured that the correct proportions of heartwood and sapwood were included in the sample used.

The woods used are described in table I. Thus 1A = butt log of e obliqua cut early 1942, MY = centre log of e. regnons.

TABLE I.

Description of Woods.

1 e.obliqua cut early 1942

A = butt log.
B = centre log.
C = head log.

A e.obliqua cut early 1944

1 = butt log.
2 = centre log.
3 = head log.

	Wood	Approximate age in years.	Date Cut	Locality
D	casuarina (she oak)	30	18/4/46	Orford
E	atherosperma moschatum (sassafras)	70	26/4/46	Kallista
G	phyllocladus rhomboidalis (celerytop pine)	80	26/4/46	"
H	acacia melanoxylon (black wood)	50	26/4/46	"
J	e.gigantea	28	15/5/46	Mt. Lloyd
K	e.obliqua	28	1/6/46	Taranna.
L	acacia dealbata ([redacted] wattle)	20	1/6/46	"
M	e.regnans	30	26/7/46	Maydena
N	e.globulus	55	15/8/46	Buckland
O	e.viminalis	45	15/8/46	"
P	A throtaxis cupressoides or A selaginoides (King William pine)	300?	-/9/46	Yolande R. (Zeehan Road)

X = butt log
Y = centre log
Z = head log

The Percolator.

The percolation apparatus is shown in figures I and 2. Figure I illustrates the general arrangement. It consists of a Herculoy acid vessel fitted with pressure gauge and blow off valve. A copper tube delivers acid under pressure to the percolator which contains the wood to be hydrolysed.

Figure 2 gives details of the percolator itself. It consists of a ten inch copper tube of one inch diameter surrounded by an oil jacket which is fitted with oil filter and thermometer pocket. Each end is closed by a screw cap fitted with a needle valve attached to control the flow of acid. The caps are fitted with lead gaskets.

The inner tube also shown in Figure 2 was used in most percolations. It is a simple copper tube fitted with a copper flange at the lower end. Lead washers are placed on either side of the flange to prevent acid passing between the inner tube and percolator itself. A removable turned bronze filter plug is placed inside the lower end and supports an alundum filter disc which fits closely to the inner tube to prevent sawdust from being carried from the percolator.

A water condenser is fitted to the lower needle valve.

Method of Percolation.

The method used in Section A will be described first. The inner tube was not used. First the lower cap was tightly screwed onto the percolator. Thirty grams of oven dry (O.D.) shavings were then packed into it by pressing down successive small additions with a rod of the same internal diameter as the percolator. Care was taken not to lose any of the charge. The top cap was then screwed on and the condenser attached to the lower end.

The acid vessel was filled with acid of the required concentration as determined by a sulphate estimation. The amount of acid used depended on the rate of flow and the duration of the percolation. The lid of the acid vessel with its pressure gauge and blow off valve was then bolted into position and the acid vessel was lowered into the oil bath by means of a suspension rope. The acid delivery tube was attached to the upper needle valve of the percolator by nipple and collar. The blow off valve was opened and the top needle valve was shut. The oil bath was heated by gas and an electric immersion heater. When the acid boiled and displaced the air in the acid vessel the blow off valve was shut. Heating was continued until the required temperature was reached when the electric heater was shut off. The temperature of the oil bath was maintained by gas ($\pm$ 5° c.) so that the gauge pressure corresponded to the temperature required in the percolator.

The oil jacket of the percolator was then heated with the gas heater shown in Figure 1 and was held at the required temperature (± 3° c.) The bottom needle valve was closed and the top needle valve was opened wide. After about thirty seconds the bottom valve was opened and hydrolysate allowed to pass through the condenser at the required rate and into a graduated cylinder. Time was measured from the instant at which the bottom valve was opened until it was shut at the end of the percolation. Immediately the bottom valve was shut all heaters were turned off and the top valve was shut.

The blow off valve was opened and the percolator detached from the rest of the apparatus. It was immediately cooled in cold water. The top cap was then removed and then the bottom valve over a large basin. The contents of the percolator were washed out and filtered through two filter papers. The residue was washed free of acid and dried overnight in an air oven at 105° c.

For the percolations of section B and C of this work the method was modified by packing 15 g. O.D. wood into the inner tube shown in Figure 2. The inner tube is placed inside the percolator and then the same procedure was used.

In Sections A and B the acid delivery tube was not lagged but it is considered that any temperature drop would be nullified by the fact that the acid would be heated in the percolator itself before it reached the wood as the latter did not occupy the full length of the percolator.

Methods of Analysis.

The Hydrolysate.

Preservation.

Wardrop (13) found that small concentrations of benzoic acid are sufficient to completely inhibit the growth of fungus which appears in the hydrolysates if they are not so treated. This was done on the day the hydrolysate was prepared.

Before analysis the hydrolysate must be steam distilled to remove furfural. No furfural is left when a negative reaction is obtained with aniline acetate paper.

After-Hydrolysis.

It was found that steam distilled hydrolysateswere not completely hydrolysed to simple sugars. For this reason the sample on which total reducing sugars was to be determined was refluxed for one hour at 100° c. after having been made to 1% with respect to sulphuric acid. This time was determined by boiling a hydrolysate obtained by percolation at 140° for various times as shown in Table II. One hour was also found to be satisfactory for hydrolysates obtained at higher temperatures.

TABLE II.

Time of Boiling (Minutes)	Munson Walker Sugar Estimation ceric sulphate titre.
0	33.9
60	44.95
131	44.65
190	45.05

Total reducing sugars. This estimation was made on an aliquot of hydrolysate which had been steam distilled and refluxed for one hour with 1% H_2SO_4 as described above. The method used was that of Munson and Walker[14]. The cuprous oxide was dissolved in acid ferric ammomium sulphate and the ferrous ammonium sulphate so formed was titrated with ceric sulphate using xylene cyanol FF as indicator[14].

The amount of cuprous oxide obtained when 64 mg. of xylose was subjected to the Munson and Walker procedure was .95 of that obtained from the same weight of glucose. The true total sugar value was obtained by adding .05 x pentose present.

Hexose Sugar. Hexose sugar was determined by subtracting pentose sugar from the true value for total sugar.

Total undecomposed hydrolysed pentose.

The pentose estimation involves distillation of the pentose containing hydrolysate with 12% hydrochloric acid to yield furfural which can be estimated by the bromination method of Iddles and Robbins [15]. Later in this work some thiobarbituric acid became available and the method of Mackney and Reynolds was used[16].

The distillation procedure [16] was that described in the Official and Tentative methods of the A.O.A.C., p. 362. In the bromination method of estimating furfural the distillate is made up to 500 ml. in a standard flask. 100 ml. of this solution is measured into a 500 ml. Erlenmeyer. flask and sufficient A R

hydrochloric acid and water are added to make 200 ml. of 12% hydrochloric acid. 25 mls. of decinormal $KBr - KBrO_3$ solution is pipetted into the flask which is stoppered swirled and placed in a dark place for one hour. At the end of this time 10 mls. of 10% K I solution is added and the excess liberated iodine is titrated with decinormal sodium thiosulphate. The difference between this titre and that of a blank is a measure of the furfural present.

1 ml .1N $Na_2S_2O_3$ = .0024 g. furfural.

The titre was converted to xylose by means of the equation $y = 0.477x$ obtained by distilling known quantities of xylose where y = mgs xylose. It was found that the type of distillation apparatus had little effect on the relation between titre and xylose provided the standard distillation procedure was used.

In the thiobarbituric acid method a water solution of thiobarbituric acid is added to the total furfural solution and the weight of xylose is calculated from the weight of furfurylidene malonyl thiourea precipitated.

furfural = .4214 T - .0012
T equals weight of precipitate.

xylose = furfural x 1.762

xylan = furfural x 1.552

These relations hold providing the weight of precipitate falls between the limits .05 to .24 gm.

Neither method is satisfactory for estimating small quantities of furfural. The bromination method includes formaldehyde and w - hydroxy methyl furfural as furfural. Formaldehyde is not included by the thiobarbituric acid method but it can only be

used when a considerable amount of furfural is present.

Table III compares results obtained by the two methods when used on a hydrolysate from a softwood or a hardwood.

TABLE III.

	Celery Top Pine	e viminalis
bromination	5.7%	14.85%
thiobarbituric acid	5.1%	14.3%

Free furfural, was estimated by the bromination method.

Free organic acids. No satisfactory method for estimating total free organic acids has been found. The conductometric titration method used by Ralph and Wardrop (17) was found to be unsatisfactory. Calorimetric methods were of no use owing to a darkening of the hydrolysate near the end point. Variable amounts of copper sulphate were also present in the hydrolysate owing to the action of the dilute acid on the copper percolator. This caused the formation of a green precipitate near the end point.

It was decided to carry out all titrations by plotting pH against titre of caustic soda. Figure 13 shows the plot of pH against titre of .172N sodium hydroxide solution for an artificial solution containing .2656g $CuSO_4 \cdot 5H_2O$ sulphuric acid and acetic acid in a volume of about 80 ml.

Point A is the theoretical end point for sulphuric acid alone and B for sulphuric and acetic acid. D is the point at which a sharp increase in pH would be expected if sodium hydroxide completely converted copper sulphate to copper hydroxide. Actually the sharp increase occurs at C.

Combined $CuSO_4$ and H_2SO_4 are calculated by sulphate estimation. Then equivalents of acid calculated from D minus equivalents of sulphate would give exactly the number of equivalents of organic acid. Actually point C was used instead of D as the sharp increase in pH occurred at C. Hence all values given for organic acids are low and only approximate. The method is of no use for calculating small quantities of organic acids. All values are calculated as acetic acid although formic acid, acetic acid and unidentified acids may be present.

The Residue.

Total loss is determined by weighing the oven dried residue and expressing it as a percentage of the original wood.

Determination of 72% H_2SO_4 Insoluble Fraction.

The lignin in the wood is not markedly altered by the percolation process excepting at high temperatures. Hydrolysis of methoxyl groups occurs but no pyrolysis has ever been observed. Xylan fission products, furfural and extraneous materials are removed fairly rapidly from the percolator so that condensation to form insoluble materials (18) is not as extensive as it was in the autoclaving experiments of Ralph and Wardrop (17).

The method of the C.S.I.R. (19) for estimating lignin was used without any of the pre-extractions used to remove extraneous materials since these had been largely removed as just mentioned.

The residue was milled through a 1 mm sieve in the Wiley mill after determining total loss. It was then oven dried and samples were weighed out for the determination of 72% H_2SO_4 insolubles and for the determination of saccharification value (see below). All weighings were carried out in weighing bottles to prevent error caused by absorption of moisture.

It is realised that some degradation might be caused by oven drying the lignocellulose residue but this could not be avoided as there was insufficient material available for moisture estimations.

15 ml of 72% sulphuric acid is added slowly with constant stirring. When the wood and acid are thoroughly mixed the weighing bottle is closed and is then left standing in a water bath at $20^\circ \pm 3^\circ$ C for two hours during which time the contents are frequently stirred. The mixture is then transferred to a 1 litre Erlenmeyer flask and diluted to 570 ml with cold water some of which is used to rinse out the weighing bottle. The mixture should now contain 3% sulphuric acid by weight. The flask is fitted with a reflux air condenser and the contents are brought to boiling point over a gas flame and are boiled gently for 4 hours. The residue is filtered on a weighed alundum crucible (RA98) and washed with 500 ml hot distilled water. It is dried in an air oven overnight and weighed.

Saccharification Value.

The method used is that of Saemen Bubl and Harris (20). To the oven dry sample in a weighing bottle is added 7½ ml 72% sulphuric acid that had been cooled to 15° C. It is thoroughly stirred with a stirring rod and put in a water bath at 30° C. This temperature is maintained for 45 minutes and the mixture is stirred at 5 - 10 minute intervals. The mixture is then washed into a 500 Erlenmeyer flask and made to 3% sulphuric acid. It is refluxed for 4½ hours. The solution is then filtered, the residue is washed and the filtrate and washings are neutralised with sodium hydroxide and made to 250 ml. Reducing sugar is determined by the Munsen and Walker method.

This method was used in Section C. In Section B, the saccharification value of the residue was estimated as 100% of the 72% H_2SO_4 soluble portion of the residue.

SUMMARY TO SECTION A.

A time series of percolations on a head log sample of e. obliqua at 140°C. showed principally a hydrolysis of the hemicellulose portion of the wood.

In the temperature series of percolations the attack was mainly on the hemicellulose portion of the wood up to 160°C. At temperatures from 160° to 200°C. both hemicellulose and true cellulose were hydrolysed with high yields of sugar.

SECTION A.

PRELIMINARY PERCOLATION EXPERIMENTS - EFFECT OF TIME AND TEMPERATURE.

The data presented in this section was obtained during the course of preliminary investigations as to the best method of operation of the percolator. The wood A3 was packed directly into the percolator as previously described. This resulted in the wood shavings at the lower end of the percolator not being attacked to quite the same extent as in the rest of the percolator since the heating jacket did not surround that region (see Fig. 2).

Table IV and Fig. 4 illustrate the effect of time of percolation at 140°C. on wood A3 using 1% H_2SO_4. A constant acid : wood ratio of 20;1 was used, i.e. 600 mls. of acid. It must be borne in mind that the constant quantity of acid resulted in vastly different rates of flow for different times. It will be shown in Section B that rate of flow has little effect on speed of hydrolysis, but has some effect on the amount of simple sugar that is decomposed.

In Fig. 4 are plotted the data of Table IV.

(1) Unhydrolysed pentose in residue.

(2) Total loss of original wood

(3) ≠ Yields of pentose sugar and organic acids.

≠ Organic acids are calculated as acetic acid.

TABLE IV.

INFLUENCE OF TIME ON PERCOLATION OF E. OBLIQUA (A3) WITH 1% H_2SO_4 AT 140°C. USING 600 ML. ACID IN EACH PERCOLATION. ALL VALUES ARE BASED ON 100 GRAMS OF O.D. WOOD.

Time Minutes	Wood Loss.	72% H_2SO_4 Insolubles in Residue	Pentosan in Residue	Hydrolysed Pentose	Organic Acids.
10½	22.1	22.3	6.1	11.6	2.4
18.	25.2	21.8	5.2	13.5	2.4
26	27.0	22.0	4.4	13.9	2.5
39¾	29.0	21.7	3.5	14.9	3.3
47	29.1	21.9	3.3	15.5	2.8
60	29.5	21.7	3.2	15.2	3.4
80½	30.2	22.3	2.8	15.7	4.2
88	32.1	21.6	2.6	16.2	3.6
98	31.1	21.8	2.6	16.2	4.3
120	32.5	21.8	2.0	16.5	4.5
163	34.7	21.4	1.3	17.8	4.1
219	34.7	21.7	1.2	17.7	4.5

TABLE V.

INFLUENCE OF TEMPERATURE ON PERCODATION ON E. OBLIQUA (A3) USING 1% H_2SO_4 200 ML/ FOR THREE HOURS. ALL VALUES ARE BASED ON 100 GRAMS OD WOOD

° °C TEMP.	WOOD LOSS	72%H_2SO_4 IN-SOLS. IN RES.	TOTAL SUGAR	HEXOSE SUGAR	PENTOSE SUGAR	FURFURAL	ORGANIC ACIDS (AS ACETIC)
126	27.9	21.8	16.9	1.9	15.0	-	2.6
141.5	35.1	21.6	22.6	5.0	17.6	-	4.1
147.5	37.0	21.6	24.1	6.7	17.4	2	4.5
158	38.4	22.8	25.9	8.1	17.8	.3	4.8
166	47.1	22.1	30.2	12.1	18.1	.4	4.5
173.5	56.2	22.4	41.2	24.3	16.9	.7	5.8
180	65.4	21.2	46.5	30.2	16.3	1.2	5.4
185.5	68.5	21.7	47.0	30.7	16.3	1.4	7.3
190.7	69.9	21.9	47.2	29.3	17.9	1.0	8.5
195.4	70.0	23.4	46.4	30.9	15.5	1.4	8.2
199.8	70.2	24.3	44.3	30.2	14.1	1.6	8.1

Table V and Fig. 5 illustrate the effect of temperature of percolation for 180 minutes on wood A3 using 1% H_2SO_4 and rate of flow = 200 mls. per hour.

The data of Table V are plotted in Fig. 5. There is shown -

(1) The total loss of original wood

(2) Total sugar formed

(3) Hexose Sugar

(4) Pentose sugar

(5) Organic acids

(6) Free furfural

(7) 72% H_2SO_4 insolubles in residue.

All data in this section and sections B and C are based on 100 grams of OD wood.

DISCUSSION:

The time series was carried out in order to estimate a suitable percolation time for the temperature series of percolations. From the work of Ralph and Hardrop[17] it was known that hydrolysis at 140°C consists mainly of an attack on hemicellulose. In Fig. 4 the total loss curve represents the amount of hemicellulose and extraneous materials removed from the wood. It is closely paralleled by the pentose sugar yield and both reach a maximum after 160 minutes. Unfortunately hexose figures are not available for this series of percolations. Hexose was determined, but the results were found later to be of no use because the hydrolysates had not been refluxed to complete hydrolysis to simple sugars. The fact that the total loss curve levels out in this manner indicates that the true cellulose is almost entirely unattacked at 140°C.

The organic acid which is largely acetic* rises to a maximum after 80 minutes. It probably arises from hydrolysis of acetyl groups associated with hemicellulose or the true cellulose or both(21).

The curve for unhydrolysed pentose shows that 2% pentose is retained in the wood after 200 minutes. Although the bromination method of Iddles and Robbins gives values which are high, the error is only of the order of ½ - 1%, it is therefore considered that a very small but definite amount of pentosan must be very closely associated with the true cellulose. Further evidence for this concept will be presented in Section C.

Figure 5 provides a great deal of useful information.

The temperature at which the attack on true cellulose commences is about 160° as was found by Ralph and Wardrop in the dilute acid autoclaving of wood(17). This is reflected in the marked inflection of the total loss, and hexose sugar curves at that temperature. Up to 170° the Hexose curve closely parallels the total loss curve but above this temperature decomposition of hexose sugar is considerable as shown by the fact that the curves are no longer similar. The amount of sugar decomposed is largely a function of the rate of flow of acid. If the acid flowed faster more sugar would be removed before it could be decomposed.

The 72% H_2SO_4 insolubles remain constant up to 190°C. This indicates that condensation of lignin with substances such as furfural must be small compared to that occurring in the autoclaving of Ralph and Wardrop(17). Above 190°C. it is probable that some pyrolysis occurs although it was not apparent in the residue. This would account for the increase in 72% H_2SO_4 insolubles above 190°C.

* See Section D.

Pentose sugar yields are maximum at 150°C. Above that temperature some decomposition takes place and is reflected in the yield of free furfural.

An increase in the yield of organic acid is associated with the decomposition of hexose.

SUMMARY TO SECTION B.

The effect of rate of acid flow (100-300 mls. per hour) acid concentration (½-2%) and temperature (162-173°C) on the hydrolysis of e. obliqua in a percolator has been studied. The hydrolysis of the "more resistant cellulose has been found to be a reaction of the first order.

Rate of acid flow has little effect on rate of hydrolysis but exerts a large effect on the amount of sugar decomposition.

Doubling the acid concentration causes a 171% increase in rate of hydrolysis.

A 10° increase in temperature between 162-183°C. causes a 100% increase in rate of hydrolysis.

These conclusions have been made from a consideration of sugar yields.

SECTION B.

THE KINETICS OF HYDROLYSIS OF E. OBLIQUA WITH DILUTE SULPHURIC ACID IN A PERCOLATOR.

NOTE: The experimental data of this section was obtained by M.H.R. Shipp, B.Sc., and C.G. Ingles, B.Sc. The conclusions derived are the work of the author. Shipp and Ingles calculated hexose sugar by subtracting pentose sugar from total sugar, but they considered the reducing power of hexose and pentose to be the same for the same weight of sugar.

EXPERIMENTAL: All Wood Al was used in all cases. All percolations were carried out on sawdust packed in the inner tube as previously described. The hydrolysates were collected in fractions of 100 mls. or 200 mls. and each fraction was treated as a separate hydrolysate. All the fractions were filtered through the same filter paper which was also used to filter the residue. Thus any solids present in the fractions of the hydrolysate are included in the residue. The filter was washed after filtering each fraction and the washings were included with each fraction. The fraction was then steam distilled and analysed in the usual way.

The following percolations were carried out using 1% H_2SO_4 for for 180 minutes:-

Rate of acid flow	temperature	
100 ml/hr	162°C 173.5°C 183°C.	3 100 ml fractions
200 ml/hr	162°C 173.5°C 183°C	6 100 ml fractions
300 ml/hr	162°C 173.5°C 183°C	9 100 ml fractions.

Percolations using varying concentrations of acid at 300 ml/hour for 180 minutes:-

173.5°C.	½% H_2SO_4)	
	1% ")	fractions 1, 2, 3, of 100 mls.
	2% ")	
183°C.	½% ")	
	1% ")	fractions 4, 5, 6, of 200 mls.
	2% ")	

Tables VI to XI give the values of hexose pentose and total sugar for each of the fractions of each percolation. Table XII gives the composition of the residues and Table XIII the composition of the original wood. The data of tables XIV to XVII was derived from the total sugar values in Tables VI and IX by the author and is presented in Figures 6 - 10. Figures 6 - 10 show straight lines obtained by plotting the logarithm of potential sugar in wood against time of percolation.
5

Figures 6, 7 and 8 illustrate the effect of rate of acid flow at various temperatures and figures 9 and 10 the effect of acid concentration at two temperatures.

To demonstrate the manner in which the data of Tables XIV to XVII was derived, consider the percolation at 183°C using 200 ml 1% H_2SO_4 per hour for three hours. After 30 minutes the first fraction of 100 ml is collected. However, at the instant at which 30 minutes has been completed there is still an amount of sugar in the percolator. The liquid capacity of the percolator between the lower valve and the filter disc is 7c.c. It will take two more minutes for this amount of sugar to flow out of the percolator.

There is also some sugar solution mixed with the wood. The 15 gms of wood is packed into a volume of about 45 mls., i.e. about 4½" of the inner percolator tube whose capacity is 10 mls. per inch. Suppose that at the instant at which 30 minutes is completed there is x gms of acid in the top ½" of wood. Then there is 2 x gms in the second ½", and so on down

to 9 x gms in the last $\frac{1}{2}$" of wood. Then the total sugar in the solution mixed with the wood is 45 x gms.

The volume of solution mixed with the wood is taken to be 45 - 15 = 30 mls., i.e. the volume occupied by wood - weight of wood. The volume associated with each $\frac{1}{2}$" of wood in the percolator is $3\frac{1}{3}$, c.c. ~~which contains 9 x gms of sugar~~. Since the rate of flow of acid is $3\frac{1}{3}$ c.c. per minute 9 x gms of sugar leave the wood in one minute and it will take 5 minutes for an amount of sugar equal to 45 x gms. to leave the percolator.

This five minutes together with the two minutes required for the sugar between the filter disc and lower valve makes a total lag of seven minutes. This conclusion is based on the following assumptions:

(1) That mixing of the sugar in upper and lower portions of wood does not take place.

(2) That decomposition of simple sugars is small.

(3) That the rate of sugar formation is constant over a short period of time.

The lag of seven minutes may be viewed in another way. The sugar collected after 30 minutes represents that formed after 23 minutes, that collected after 60 minutes as being formed at 53 minutes and so on.

For a rate of flow of 100 ml per hour the lag is 15 minutes and for 300 mls per hour it is 5 minutes.

Thus for the percolation at 183° using 200 ml. 1% H_2SO_4 per hour for three hours we have -

FRACTION	COLLECTED AFTER (MINUTES)	REPRESENTS SUGAR FORMED AFTER (MINUTES)	SUGAR IN FRACTION
1	30	23	22.3
2	60	53	7.3
3	90	83	7.2
4	120	113	6.8
5	150	143	5.1
6	180	173	3.1

≠ Potential sugar in residue + sugar in residue washings = 12.7

Hence potential sugar in wood after 173 minutes = 12.7
" 143 12.7 + 3.1 = 15.8
113 15.8 + 5.1 = 20.9
83 20.9 + 6.8 = 27.7
53 27.7 + 7.2 = 34.9
23 34.9 + 7.3 = 42.2
0 42.2 + 22.3=64.5

ALL RESULTS ARE BASED ON 100 gms OD WOOD.

≠ Shipp and Ingles did not carry out estimations of the saccharification value of the residue. Since it was essential for these derivations the value was taken to be 100% of the 72% H_2SO_4 soluble portion of the residue. If the 72% H_2SO_4 soluble portion was pure cellulose 111% would be the true value. The result so obtained for the residues described in Section C checked fairly well with the saccharification value estimated by the quantitative saccharification procedure.

TABLE VI. - TOTAL SUGAR.

Mls per Hour	Temp ^{o}C	Acid Strength	1	2	3	4	5	6	7	8	9	Total	Residue Washings
100	162	1%	19.0	3.8	2.0							24.8	0.7
"	173.5	"	24.2	7.9	6.5							38.6	2.6
"	183	"	28.2	13.1	7.1							48.4	1.6
200	162	1%	19.9	3.9	1.5	1.4	1.7	1.9				30.3	2.4
"	173.5	"	20.9	5.3	3.1	3.0	2.7	3.3				38.3	1.8
"	183	"	22.3	7.3	7.2	6.8	5.1	3.1				51.8	2.7
300	162	1%	12.8	6.2	2.1	2.0	1.3	1.5	1.1	1.3	1.2	29.5	1.9
"	173.5	"	19.4	4.6	3.1	2.3	2.4	2.6	2.2	2.3	2.0	40.9	3.0
"	183	"	21.0	7.6	6.3	5.1	3.4	3.7	2.8	2.0	1.8	53.7	5.9

TABLE VII - PENTOSE.

Mls. per Hour	Temp ^{o}C	Acid Strength	1	2	3	4	5	6	7	8	9	TOTAL
100	162	1%	11.2	1.5	1.3							14.0
"	173.5	"	12.4	0.8	0.4							13.5
"	183	"	11.6	0.7	0.4							12.7
200	162	1%	12.2	1.6	0.3							14.1
"	173.5	"	12.2	1.0	0.3	0.2	0.1	0.2				14.0
"	183	"	12.6	1.0	0.5	0.4	0.2	0.1				13.8
300	162	"	5.5	4.8	1.2	0.6	0.3	0.3	0.2	0.2	0.2	13.3
"	173.5	"	11.2	1.9	0.4	0.2	0.1	0.1	0.1	0.1	0.1	14.2
"	183	"	12.7	1.4	0.4	0.3	0.2	0.1	0.2	0.1	0.1	15.5

TABLE VIII - HEXOSE SUGAR.

Mls Per Hour	Temp °C	Acid Strength	1	2	3	4	5	6	7	8	9	Total
100	162	1%	7.9	2.2	0.7							10.8
"	173.5	"	11.8	7.1	6.1							25.0
"	183	"	16.6	12.4	6.7							35.7
200	162	"	7.7	2.3	1.2	1.4	1.7	1.9				16.2
"	173.5	"	8.7	4.3	2.8	2.8	2.6	3.1				24.4
"	183	"	9.7	6.4	6.6	6.4	5.0	3.0				37.1
300	162	"	7.4	1.4	0.9	1.4	1.0	1.2	0.9	1.0	1.0	16.2
"	173.5	"	8.3	2.8	2.7	2.1	2.2	2.5	2.1	2.2	1.9	26.8
"	183	"	8.3	6.2	5.8	4.8	3.2	3.6	2.6	1.9	1.7	38.7

TABLE IX. - TOTAL SUGAR.

Mls. per Hour	Temp °C	Acid Strength	1	2	3	4	5	6	Total	Residue Washings
300	173.5	½%	19.4	3.8	2.4	2.7	3.3	2.3	33.9	3.2
"	"	1%	19.4	4.6	3.1	4.7	4.8	4.2	40.8	2.0
"	"	2%	28.7	9.1	4.7	8.3	4.5	3.3	58.6	3.2
"	183	½%	22.9	5.9	4.3	7.5	5.8	3.2	49.6	6.6
"	"	1%	21.0	7.6	6.3	8.4	6.5	3.8	53.6	5.9
"	"	2%	28.7	11.0	4.5	7.7	3.3	0.9	56.1	0.5

TABLE X - PENTOSE SUGAR.

Mls per Hour	Temp °C	Acid Strength	1	2	3	4	5	6	Total
300	173.5	½%	11.7	1.8	0.4	0.5	0.4	0.3	15.1
"	"	1%	11.2	1.8	0.4	0.3	0.2	0.2	14.1
"	"	2%	11.9	0.3	0.2	0.3	0.2	-	12.9
"	183	½%	12.7	1.0	0.3	0.3	0.3	0.3	14.9
"	"	1%	12.7	1.4	0.4	0.4	0.3	0.2	15.4
"	"	2%	11.0	1.7	0.3	0.4	0.3	-	12.7

TABLE XI - HEXOSE SUGAR.

Mls per Hour	Temp °o	Acid Strength	1	2	3	4	5	6	Total
300	173.5	½%	7.7	2.0	2.0	2.1	3.0	2.0	18.8
"	"	1%	8.3	2.8	2.7	4.4	4.6	4.0	26.7
"	"	2%	17.7	8.8	4.5	8.0	4.4	3.3	45.7
"	183	½%	10.3	4.9	3.9	7.2	5.5	2.9	34.7
"	"	1%	8.3	6.2	5.8	8.0	6.2	3.6	38.1
"	"	2%	17.7	10.3	4.2	7.3	3.1	0.9	43.5

TABLE XII.

ANALYSIS OF RESIDUES.

~~(Methods described by Reference (19))~~

CONDITIONS OF PERCOLCATION.			RESIDUE	72% H_2SO_4 INSOLUBLES CALC. ON O.D. WOOD	72% H_2SO_4 SOLUBLES CALC. ON O.D. RESIDUE	POTENTIAL SUGAR IN RESIDUE	PENTOSAN	WOOD LOSS
TEMP. °C	RATE MLS PER Hour	Acid STRENGTH						
162	100	1%	61.0	21.1	34.6	39.8	1.15	39.0
	200		52.2	17.9	34.4	34.2	1.22	47.8
	300		51.0	16.9	33.1	34.2	1.23	49.0
173.5	100	1%	43.8	21.2	48.4	22.6	0.91	56.2
	200		43.4	19.3	44.4	24.1	0.99	56.6
	300		43.2	19.1	44.2	24.1	1.00	56.8
183	100	1%	30.4	20.5	67.5	9.9	0.61	69.6
	200		29.9	19.9	66.6	10.0	0.73	70.1
	300		29.1	19.3	66.5	9.7	0.84	70.9
173.5	300	½%	48.9	18.1	36.9	30.8	1.70	51.1
		2%	25.9	21.2	82.5	4.5	0.87	74.1
183	300	½%	34.6	19.5	56.5	15.0	1.04	65.4
		2%	25.8	23.4	90.3	2.5	0.84	74.2

TABLE XIII.

ANALYSIS OF WOOD Al (Methods described by reference (19)).

HOT WATER SOLUBLE	N/25N2OH SOLUBLE	HOLOCELLULOSE	CROSS AND BEVAN CELLULOSE	PENTOSAN	LIGNIN	HOT WATER SOLUBLES
11.2	19.28	70.85	54.5	14.19	20.50	11.2

TABLE XIV.

POTENTIAL SUGAR IN WOOD.

MLS PER HOUR	TEMP °C	ACID STRENGTH	0	45	105	165
100	162	1%	65.3	46.3	42.5	40.5
"	173.5	"	63.8	39,6	31.7	25.2
"	183	"	59.9	31.7	18.6	11.5

TABLE XI

POTENTIAL SUGAR IN WOOD.

MLS PER HOUR	TEMP °C	ACID STRENGTH	0	23	53	83	113	143	173
200	162	1%	66.9	47.0	43.1	41.6	40.2	38.5	36.6
"	173.5	"	63.6	42.7	37.4	34.3	31.3	28.6	25.3
"	183	"	64.5	42.2	34.9	27.7	20.9	15.8	12.7

TABLE XVI.

POTENTIAL SUGAR IN WOOD.

MLS PER HOUR	TEMP °C	ACID STRENGTH	0	15	35	55	75	95	115	135	155	175
300	162	1%	65.7	52.9	46.7	44.5	42.5	41.2	39.7	38.6	37.3	36.1
"	173.5	"	67.0	47.6	43.0	39.9	37.6	35.2	32.6	30.4	28.1	26.1
"	183	"	69.3	48.3	40.7	34.4	29.3	25.9	22.2	19.4	17.4	15.6

TABLE XVII.

POTENTIAL SUGAR IN WOOD.

MLS. PER HOUR	TEMPERATURE °C	ACID STRENGTH	0	15	35	55	95	135	175
300	173.5	½%	67.9	48.5	44.7	42.3	39.6	36.3	34.0
"	"	2%	66.3	37.6	28.5	23.8	15.5	11.0	7.7
"	183	½%	71.2	48.3	42.4	38.1	30.6	24.8	21.6
"	"	2%	59.1	30.4	19.4	14.9	7.2	3.9	3.0

DISCUSSION:

The graphs of log potential sugar in wood plotted against time of percolation (Figures 6-10) are all straight lines and so indicate a reaction of the first order for the more resistant portion of the cellulose. The first order reaction constant k for each set of conditions is given by the equation.

$$k = \frac{2.303}{t_2 - t_1} (\log a_1 - \log a_2)$$

where a_1 = potential sugar in wood at t_1 minutes

a_2 = " " " " t_2 "

The different values of k for different conditions are given in table XVIII.

TABLE XVIII.

Temperature °C.	Acid Strength	Rate of Acid Flow	k The First Order Reaction Constant.
162	1%	300 mls/hr	.0018
162	1%	200	.0012
162	1%	100	.0011
173.5	1%	300	.0035
173.5	1%	200	.0030
173.5	1%	100	.0037
183	1%	300	.0071
183	1%	200	.0084
183	1%	100	.0084
173.5	½%	300	.0019
173.5	2%	300	.0094
183	½%	300	.0054
183	2%	300	.0175

It is to be emphasised that these values only apply to the hydrolysis of the more resistant portion of the cellulose. Tables VII and X show that almost all the pentose yielding material is hydrolysed in the first few minutes of the percolation and the yield of sugar obtained in the first fraction is much greater than that required for a first order

reaction.

Saeman (9) has shown that the decomposition of simple sugars with dilute acid is a first order reaction. Hence the amount of sugar decomposed in a given time inside the percolator is directly proportional to the amount of sugar present in the percolator. This latter is proportional to the first order reaction constant for the hydrolysis. Therefore the slope of the graphs in figs. 6-10 will not be altered by sugar decomposition and the true reaction constants for hydrolysis of the resistant cellulose must be obtained from a consideration of sugar yields.

Decomposition of sugars will cause a vertical displacement of the graphs and the intercept on the y axis should be lowered. Decomposition is greater at 183° than at 162°. Hence for a given rate of acid flow the intercept for 162° should be greater than for 183°. (see Fig 6 7 and 8) This is the case using 100 ml/hr. acid flow. That it is not the case for 200 ml/hr and 300 ml/hr. must be ascribed to error in the value taken for saccharification value of the residues. It has already been mentioned that the value is an approximation.

Effect of rate of acid flow on hydrolysis rate.

Table XVIII shows that variation of rate of acid flow has little effect on the rate of hydrolysis. Its effect on decomposition of sugars has already been discussed

Effect of acid concentration.

Figure 11 gives the graph of log k against log acid concentration for 173.5° and 183°C. The values for ½%

acid are anomalous* but the other values give straight lines the slopes of which are both 1.44. This corresponds to an increase of 171% in rate of hydrolysis with 100% increase in acid concentration. Saeman (9) obtained an increase of 153% with 100% increase in acid concentration when he hydrolysed Douglas fir in sealed glass bombs.

Effect of Temperature.

Figure 11 also gives the graph of log k against the reciprocal of the absolute temperature. Again the values of log k at $\frac{1}{2}$% acid are anomolous but the graphs for 1% acid and 2% acid are parallel and may be considered to obey the Arrhenius equation.

$$\log k = \frac{-E}{2.303\ RT} + \text{constant}$$

whence it is found that E the energy of activation equals 26,500 calories. A 10° rise in temperature causes an increase in the rate of hydrolysis of about 100% between 162° and 183°C.

Again it is interesting to compare Saeman's results. He gave an energy of activation of about 43000 calories and found that a 10° rise in temperature over the range 170° to 190°C. increases the reaction rate by 186%. Since it is known that the amount of acetic and formic acid formed by hydrolysis of wood in closed vessels (17) increases with increasing temperature it is suggested that the marked difference between the results of Saeman and those here presented might be due to an increase in rate of hydrolysis

* That values of k for $\frac{1}{2}$% acid do not fit in with other values is considered to be due to error in the saccharification value of the residue. The saccharification value is an approximation and where it is of the order of 25 as in this case large errors are possible.

caused by the presence of these acids. In percolation any acetic or formic acid is carried away so that it can have little effect on the rate of hydrolysis.

Particle Size.

No investigation has been carried out on the effect of particle size on reaction rate. The largest particle size in the wood samples was the aperture of the 14 mesh BSS seive (.035"). Saeman (9) hydrolysed Douglas fir samples of 20-40 mesh (presumably U.S. sieve series) and hence his largest particle size was .033". He found that this particle size was hydrolysed at the same rate as smaller sizes.

Optimum Conditions.

There is really no such thing as an optimum set of conditions for production of hexose sugar or of total sugar. A perusal of tables VI to XI shows that there are many sets of conditions giving high yields. The higher the temperature and the stronger the acid the faster the cellulose is attacked but these conditions also cause a high rate of sugar decomposition and therefore it is necessary to increase the rate of acid flow to obtain high sugar yields.

Pentose Yields.

The pentose yields are little affected by the conditions of hydrolysis. The yields are slightly lower when the rate of acid flow is 100 ml/hr than when it is 300 ml/hour.

Pentose was estimated by the bromination method and it is considered that the values for hydrolysate fractions after the first are definitely higher than the true value.

SUMMARY TO SECTION C.

The rate of hydrolysis of the "more resistant cellulose" in specimens of eleven different Tasmanian woods is compared. In all cases the hydrolysis is a first order reaction and the first order reaction constants have been calculated.

SECTION C.

Dilute Acid Hydrolysis of Various Tasmanian Woods with a Percolation Apparatus.

Experimental.

The sawdust samples used were prepared from a middle log of each timber. The method of percolation was that which has been described previously. The following conditions were chosen for all percolations.

Temperature	:	173.5°C.
Rate of acid flow	:	300 mls per hour.
Strength of acid	:	2%
Time	:	180 minutes.

These conditions were chosen since it was found in section B that they gave a high yield of sugar, however any other set of conditions which causes an appreciable attack on the more resistant cellulose would have been equally satisfactory for comparing the different woods. The first three fractions of 100 ml. were collected at 20 minute intervals and the last three of 200 mls at 40 minute intervals. The composition of the various fractions for the percolation of each wood is given in Table XIX. Values for total sugar, pentose sugar, furfural and organic acids are shown. In some cases pentose sugar was estimated by the thiobarbituric acid method. Pentose estimations were carried out by this method on mixtures of 1st only, 1st + 2nd fraction, 1st + 3rd + 4th.

This technique overcame the fact that pentose in the second fraction was insufficient to be estimated by itself. No pentose was indicated in the other fractions by this method. Distillation of fractions 3, 4, 5, 6 of the hydrolysates from e. regnans, e.obliqua, e. viminalis, e.globulus, sassafras, celery, top pine and King William pine with 12%

hydrochloric acid gave furfural which coloured aniline acetate. Therefore pentose must be present in traces in the 3rd, 4th, 5th and 6th fractions.

Organic acid was found in fractions one and two but the method used was not capable of estimating small quantities which were undoubtedly present in the remaining fractions.

The compositions of the residues are given in Table XX. The saccharification value of the residue was determined by the quantitative saccharification procedure of Saeman, Bubl and Harris (20).

The total potential reducing sugar in the wood after various time intervals is given in Table XXI. The logarithm of potential sugar in wood is plotted against time for each wood in figures 12, 13, 14, 15 and 16.

A graph of potential sugar in e.regnans for various times was obtained by considering the weight of residue left after percolation with 2% acid at 300 mls per hour. The residues were weighed (O.D.) and the saccharification of one of them was determined. The weight of material which did not yield sugar was subtracted from the weights of each of the other residues to give the amount of cellulose contained in them and hence the amount of glucose obtainable from each residue. These values are given in table XXIII and are plotted in figure 19.

All results are based on 100 g. O.D. wood.

TABLE XIX.

DETAILS OF HYDROLYSATE FRACTIONS.

173.5°C. 300 mls. per hour 2% H_2SO_4 180 minutes

WOOD		100 ml. fractions 1	2	3	200 ml. fractions 4	5	6	TOTAL
e.regnans	TOTAL SUGAR	24.2	7.3	4.7	8.6	7.4	4.1	56.3
	PENTOSE "	+16.5	-					16.5
	FURFURAL	0.42	0.15					0.57
	ORGANIC ACID	4.3	-					4.3
e.obliqua	TOTAL SUGAR	22.8	8.0	4.9	9.5	5.2	4.9	55.3
	PENTOSE "	+15.4	0.2					15.6
	FURFURAL	0.2	0.07					0.27
	ORGANIC ACID	3.8	.4					4.2
e.viminalis	TOTAL SUGAR	28.3	6.3	3.2	9.2	6.9	3.8	57.7
	PENTOSE "	+14.3	0.3					14.6
	FURFURAL	0.50	0.07					0.57
	ORGANIC ACID	4.4	.2					4.6
e.globulus	TOTAL SUGAR	31.7	6.4	3.8	8.6	5.4	3.3	59.2
	PENTOSE "	+19.5	0.2					19.7
	FURFURAL	0.97	0.06					1.03
	ORGANIC ACID	5.7	.2					5.9
e.gigantea	TOTAL SUGAR	27.6	7.0	6.1	9.1	6.6	2.6	59.0
	PENTOSE "	19.3	.6					19.6
	FURFURAL	0.70	0.07					0.77
	ORGANIC ACID	5.0	0.82					5.8
Atherosperma Moschatum (Sassafras)	TOTAL SUGAR	27.7	5.4	4.8	7.5	6.8	4.6	55.8
	PENTOSE "	+20.1	0.7					20.8
	FURFURAL	0.46	0.05					0.51
	ORGANIC ACID	4.7	.5					5.2
Silver Acacia Dealbata (Silver Wattle)	TOTAL SUGAR	30.7	6.4	5.2	7.9	6.2	4.3	60.7
	PENTOSE "	21.1	0.9					22.0
	FURFURAL	0.47	0.05					0.52
	ORG. ACID	5.1	0.2					5.3
Acacia Melanoxylon (Blackwood)	TOTAL SUGAR	26.1	7.7	5.8	9.5	4.3	2.6	56.0
	PENTOSE "	20.3	0.7					21.0
	FURFURAL	0.42	0.05					0.47
	ORGANIC ACID	5.1	0.2					5.3
Casuarina (Sheoak)	TOTAL SUGAR	23.9	5.5	3.7	7.4	3.9	2.9	47.3
	PENTOSE "	19.5	0.7					20.2
	FURFURAL	0.31	0.09					0.40
	ORGANIC ACID	5.1	.2					5.3

Table XIX continued.

WOODS		1	2	3	4	5	6	TOTAL
Celery Top Pine	Total Sugar	22.5	6.3	6.0	9.0	5.3	2.5	51.6
	Pentose "	5.1	0.6					5.7
	Furfural	0.17	0.02					0.19
	Organic Acid	1.9	.2					2.1
King William Pine	Total Sugar	21.0	5.7	4.1	7.3	5.0	4.1	47.2
	Pentose "	6.5	0.1					6.6
	Furfural	0.17	0.05					0.22
	Organic Acid	1.7	.2					1.9
(Second Percolation).								
e.obliqua	Total Sugar	21.6	6.5	5.1	7.8	7.9	4.1	53.0

+ Pentose estimated by the thiobarbituric acid method.

TABLE XX.

DETAILS OF PERCOLATION RESIDUES.

173.5°C. 300 mls. Per Hour 2% H_2SO_4 180 minutes.

	RESIDUE	72% H_2SO_4 INSOLUBLES	SACCHARIFICATION VALUE	SUGAR IN RESIDUE WASHINGS
e. regnans	27.1	15.5	11.2	0.5
e. obliqua	32.5	17.6	14.5	1.6
e. viminalis	26.4	17.1	8.0	1.3
e. globulus	24.0	16.1	6.6	1.7
e. gigantea	22.0	16.4	3.9	0.9
Atherosperma Moschatum (Sassafras)	26.8	15.7	10.5	1.1
Acacia Dealbata (Silver Wattle)	22.7	16.0	7.0	0.5
Acacia Melanoxylon (Blackwood)	24.4	17.3	6.1	0.3
Casuarina (Sheoak)	28.8	20.3	8.2	0.9
Celery Top Pine	34.0	29.0	5.4	1.1
King William Pine	42.0	31.2	11.3	1.7
e. obliqua (second percolation)	30.0		14.4	1.2

TABLE XXI.

POTENTIAL SUGAR IN WOOD AT VARIOUS TIME INTERVALS.

173.5°C. 300 mls. Per Hour. 2% H_2SO_4. 180 Minutes.

	MINUTES. 0	15	35	55	95	135	175
e. Regnans	68.0	43.8	36.5	31.8	23.2	15.8	11.7
e. Obliqua	72.5	49.7	41.7	36.8	27.3	21.0	16.1
e. Viminalis	67.0	38.7	32.4	29.2	20.0	13.1	9.3
e. Globulus	67.5	35.8	29.4	25.6	17.0	11.6	8.3
e. Gigantea	63.8	36.2	29.2	23.1	14.0	7.4	4.8
Atherosperma Moschatum (Sassafras)	68.4	40.7	35.3	30.5	23.0	16.2	11.6
Acacia Dealbata (Silver Wattle)	69.5	37.8	31.4	26.2	18.3	11.8	7.5
Acacia Melanoxylon (Blackwood)	62.8	36.3	28.6	22.8	13.3	9.0	6.4
Casuarina (Sheoak)	56.9	33.0	27.0	23.3	15.9	12.0	9.1
Celery Top Pine	58.1	35.6	29.3	23.3	14.3	9.0	6.5
King William Pine	60.1	39.1	33.4	29.3	22.0	17.0	13.0
e. Obliqua (second Percolation)	68.6	47.0	40.5	35.4	27.6	19.7	15.6

TABLE XXII.

CHEMICAL COMPOSITION OF TASMANIAN HARDWOODS AND SOFTWOODS

Results expressed in Percentages of oven-dry (105°) wood.

AFTER D.L. INGLES

Wood.	Ash	Solubility in: Hot Water	Solubility in: a. Alcohol Benzene	Solubility in: Hot water of extract from a.	Solubility in: N/25 Caustic Soda	Lignin	*Holocellulose	Cross and Bevan Cellulose	Pentosans: Total	Pentosans: In Cross and Bevan Cellulose	Pentosans: Not in Cellulose	Summative Total. HOLOCELLULOSE LIGNIN EXTRACTIVES
Hardwoods.												
E. Regnans	0.30	2.0	1.5	0.6	9.2	18.3	81.8	65.2	15.9	11.4	4.5	102.5
E. Obliqua	0.25	3.3	1.4	1.8	9.7	21.7	76.4	64.9	16.2	10.4	5.8	101.5
E. Viminalis	0.16	6.5	2.9	3.5	14.5	18.3	76.9	53.3	14.5	7.0	7.5	101.7
E. Globulus	0.24	2.6	1.1	1.5	13.3	18.8	82.2	60.7	21.5	13.5	8.0	103.8
E. Gigantea	0.17	3.4	2.7	0.7	11.8	18.1	75.8	53.8	20.2	13.1	7.1	97.5
Sassafras	0.54	2.1	1.6	0.4	11.8	21.4	77.0	60.5	19.9	11.2	8.7	101.0
Silver Wattle	0.37	6.7	5.3	1.4	15.6	17.3	77.0	67.4	19.4	14.5	4.9	101.3
Blackwood	0.28	9.0	8.2	1.0	18.8	18.8	72.6	57.8	19.9	11.6	8.3	100.9
Sheoak	0.55	8.7	6.8	1.9	17.5	23.2	68.5	47.1	20.1	13.6	6.5	100.9
Softwoods.												
Celery Top pine	0.30	9.0	10.1	2.3	15.8	27.8	69.5	53.2	6.2	3.4	2.8	110.0
King William Pine	0.15	4.5	4.7	0.0	9.4	32.1	70.7	59.1	6.3	3.8	2.5	107.7

* Corrected for Residual Lignin.

TABLE XXIII.

Percolation Residues from E. Regnans.

Time (minutes).	Potential Sugar.
30	44.2
72	32.1
122	21.6
183	11.8

DISCUSSION:

The graph of log (potential sugar in wood) against time is a straight line for each wood. This is to be expected from the results obtained in section B. From the slopes of the lines the first order reaction constant has been calculated for each wood and is given in Table XXII. The constants only apply to the hydrolysis of a "more resistant cellulose" portion of the wood.

TABLE XXII.

Wood.	First Order Reaction Constant.
e. regnans	.0083
e. obliqua	.0071
e. viminalis	.0090
e. globulus	.0093
e. gigantea	.0137
atherosperma moschatum (sassafras)	.0079
acacia dealbata (silver wattle)	.0100
acacia melanoxylon (blackwood)	.0115
casuarina (sheoak)	.0077
celery top pine	.0098
King William pine	.0069

Table XXII expresses quantitatively the fact that the "more resistant cellulose" differs considerably in the different woods.

Mitchell (5) considers that western hemlock wood contains a hemicellulose portion of D.P. about 70 and a true cellulose portion of D.P. 2000-2500 without material of intermediate chain length.

The hemicellulose portion of every wood mentioned in this section has been very easily hydrolysed. This is proven by the fact that almost all the pentose yielding material of every wood was hydrolysed in the first 15 minutes of the percolation process. The hydrolysis of the remaining "more resistant cellulose" is slow and since it is a reaction of the first order the "more resistant cellulose" must be fairly homogeneous.

If hydrolysis consists essentially of the rupture of cellulose chains to give simple sugars then the rate of sugar formation and the first order reaction constant should be inversely proportional to the degree of polymerisation of the cellulose chain and the term homogeneity as applied to cellulose must include a certain amount of homogeneity in degree of polymerisation. This is considered to be evidence in support of Mitchell's theory that hemicellulose has a relatively low D.P. and is quite distinct from the alpha cellulose of high D.P.

The portion of wood cellulose which is resistant to acid hydrolysis is here called "more resistant cellulose" because it is not known whether it is exactly the same as alpha cellulose but there is not likely to be a great difference.

If rate of hydrolysis is a function of chain length it can be concluded that the average D.P. of the "more resistant cellulose" is higher in some woods than in others and the more rapid the hydrolysis the lower is the average degree of polymerisation.

Wise (21) states that cellulosan is closely associated with true cellulose and the two together he calls plant cellulose. The cellulosan chains containing xylan may be present in the micells and he considers that there are chains of varying length but that they are generally shorter than the chains of true cellulose. The cellulosan chains might contain only xylan or a mixture of xylan and glucosan units (22).

It has been mentioned that almost all the pentose yielding material is very rapidly removed from the woods considered. Hence most of the cellulosan must be rapidly

removed and should have a much lower D.P. than the true cellulose. No pentose was indicated in fractions 3, 4, 5, and 6 of the hydrolysates from e. regnans, e. viminalis, e.globulus, sassafras, celery top pine and King William pine when the thiobarbituric acid method was used, but the fact that furfural was obtained on distillation with 12% hydrochloric acid indicates that traces of pentose sugars were present in these fractions of the hydrolysates of these woods. The furfural was detected by aniline acetate paper.*

Decomposition of Sugars.

It has been stated that decomposition of sugars in the percolator is small.

A graph of potential sugar against time for e. regnans is shown in figure 12 in which the potential sugar values were obtained directly from the weights of residues. This graph (a) is parallel to the graph (b) obtained by considering sugar in the hydrolysate and this fact is confirmation of the reaction constant for hydrolysis of e. regnans calculated from (b).

The ratio of potential sugar in (b) to that in (a) for any time is about .83 which means that about 17% of the sugar formed in the percolator is decomposed.

Amount of "More Resistant Cellulose"

The amount of "more resistant cellulose is indicated by the value for potential sugar in wood at zero time.

Values for this more resistant cellulose are given below. They have been corrected for the 17% decomposition which is considered to take place, but they are only approximate. Factors which involve possible error are

1. The difficulty in controlling the temperature of the percolator to closer than 3°C.

2. The assumptions made regarding the lag in time for delivery of sugar produced after a certain time.

3. Possible cumulative errors in the determination of total sugar by the Munsen Walker method.

Wood	+ More Resistant Cellulose
e. regnans	54
e. obliqua	57
e. viminalis	48
e. globulus	43
e. gigantea	48
sassafras	50
silver wattle	48
blackwood	46
sheoak	38
celery top pine	47
King William pine	46

+ on 100 g. O.D. wood.

The chemical composition of the various woods is given in Table XXII by kind permission of D. L. Ingles B.Sc.

A comparison of the values for "more resistant cellulose" with those for Cross and Bevan cellulose in Table XXII shows that the former are generally much lower.

It would be very interesting to ascertain the amount of "more resistant cellulose" in an apparatus which could be strictly controlled and to compare the results with the values for alpha cellulose determined on the original wood.

Organic Acids (see fig. XIX).

Organic acids could be determined only on the first and second fractions owing to the restrictions of the method used. The amount of organic acid obtained in the first fraction from the two softwoods viz. celery top pine and

King William pine is much lower than from hardwoods. If this acid is mainly acetic as it is in e.obliqua (see section D) then the acetyl content of these two softwoods is less than that of the hardwoods.

72% H_2SO_4 Insolubles in the Residue and its Relation to Lignin.

A comparison of 72% H_2SO_4 insolubles given in Table XX and the values for lignin in Table XXII shows that the former are always smaller in the case of the hardwoods. This may be due to

1. Hydrolysis of methoxyl groups in the lignin.
2. Some of the lignin may dissolve in the hot acid.

The Relative Values of the Different Woods for Wood Hydrolysis.

It has been shown that some woods are hydrolysed more easily than others. However it must be remembered that only one sample of each wood has been hydrolysed in the percolator so that no general ruling can be made.

In any case the choice of any particular wood for large scale wood hydrolysis would be controlled more by its availability than its ease of hydrolysis.

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SECTION D.

SUMMARY:

(1) Some experiments on the identification of some specific sugars obtained by acid hydrolysis of e. obliqua Crystalline derivatives of mannose and xylose have been obtained as well as mucic acid.

(2) Analysis of organic acids obtained at temperatures from 140° to 200°C. in an autoclave.

INTRODUCTION:

Hydrolysis at temperatures below 150°C. consists mainly of an attack on the hemicellulose portions of the wood (see sections B. and C. of this work) which may contain hexose and pentose sugar units and uronic acids. According to Norman (1) the sugar units found in plant hemicelluloses usually belong to two distinct configurational groups. The two groups are (i) glucose series : d. glucose d. glucuronic acid and d. xylose, (ii) galactose series: d. galactose d. galacturonic acid and l. arabinose. Mannose also has been reported as a hemicellulose constituent. From the results of most analyses it appears that the glucose series predominates in hardwoods while both series are found in softwoods. For example Ritter and Kurth (2) isolated derivatives of glucose, xylose and arabinose and detected traces of fructose from the easily hydrolysable portion of spruce holocellulose. Also Sutermeister (3) states that the reducing sugars indicated in the Table I are present in jack pine, a softwood, and birch, a hardwood. They were obtained by hydrolysis of the woods with 72% sulphuric acid.

TABLE I.

	Jack Pine.	Birch
Glucose	46.4	47.9
Mannose	9.7	1.3
Galactose	4.3	0.0
Xylose	6.1	21.3
Arabinose	2.2	0.3
Total Reducing Sugar	68.7	70.8

As far as this author is aware no such evidence is available for any Australian eucalyptus and the work here presented is only of a preliminary nature in this direction. That the more resistant structural cellulose is almost entirely built of glucose units is generally recognised and the following work is confined to the easily hydrolysed hemicellulose portion of the wood.

Much less has been done on this aspect than was originally intended owing to lack of time and difficulty in obtaining chemicals during the war years.

It is also worth mentioning that whereas in the past, most investigations of hemicellulose constituents have been carried out by means of alkali extractions this author is of the opinion that hydrolysis of wood in a percolator at temperatures as low as 100° (and upwards in steps), would yield valuable information as to the structure of the hemicellulose portion of the wood.

With regard to the production of organic acids by the dilute acid hydrolysis of wood, Ralph and Wardrop [4] showed that from 130 - 160° the yield is about 4% of the weight of the wood. At temperatures above 160° the yield of organic acids rapidly increased, but no indication of the nature of these acids was given.

Ritter and Kurth [2,5,6] have shown the presence of acetyl groups in the carbohydrate portion of spruce white oak and maple andit is probable that the yield of organic acids under moderate conditions of hydrolysis is largely derived from this source. At higher temperatures the large increase in the yield of organic acids is associated with decomposition of reducing sugars.

EXPERIMENTAL.

Benzimidazole derivatives.

An attempt was made to separate the constituents of a sugar mixutre by means of the benzimidalole derivatives.[7] Wood 2A of particle size -52+72 was

extracted with hot water for one hour and about 60 g. was cooked in an autoclave under the conditions $\frac{150/40/1}{7:1}$ ≠ by the method of Ralph and Hardrop[4]. The hydrolysate was filtered and steam distilled to remove furfural. Sulphuric acid was precipitated with barium carbonate and the solution was evaporated to a small volume on a water bath after filtering off the barium sulphate. Barium salts of uronic acids were removed by pouring the solution into five times its volume of ethyl alcohol[2], Alcohol was removed by evaporation. The solution was clarified with neutral lead acetate dissolved in a minimum of water and deleaded with oxalic acid to give an almost water while solution. Excess oxalic acid must not be used owing to the possibility of precipitation of potassium oxalate with potassium salts of aldonic acids in the hypoiodite oxidation described below. The solution was then evaporated to contain about 50% reducing sugar and dissolved in 75 ml. of acetone free methanol.

This methanol solution was used for oxidation of the aldoses to aldonic acids with iodine and alkali.

It is sufficient to indicate the scheme of separation as in Table II after Moore and Link.[7]

≠ $\frac{150/40/1}{7:1}$ = 150°C. for 40 minutes using 1% H_2SO_4 with a liquid:solid ratio of 7:1.

TABLE II.

Aldo Monosaccharides

| Oxidation
| I_2 + K O H in methanol

K Salts of aldonic acids

| condense with
| o-phenylene diamine
| HCL H_3PO_4 135°C.

Benzimidazoles
from glucose
arabinose
galactose

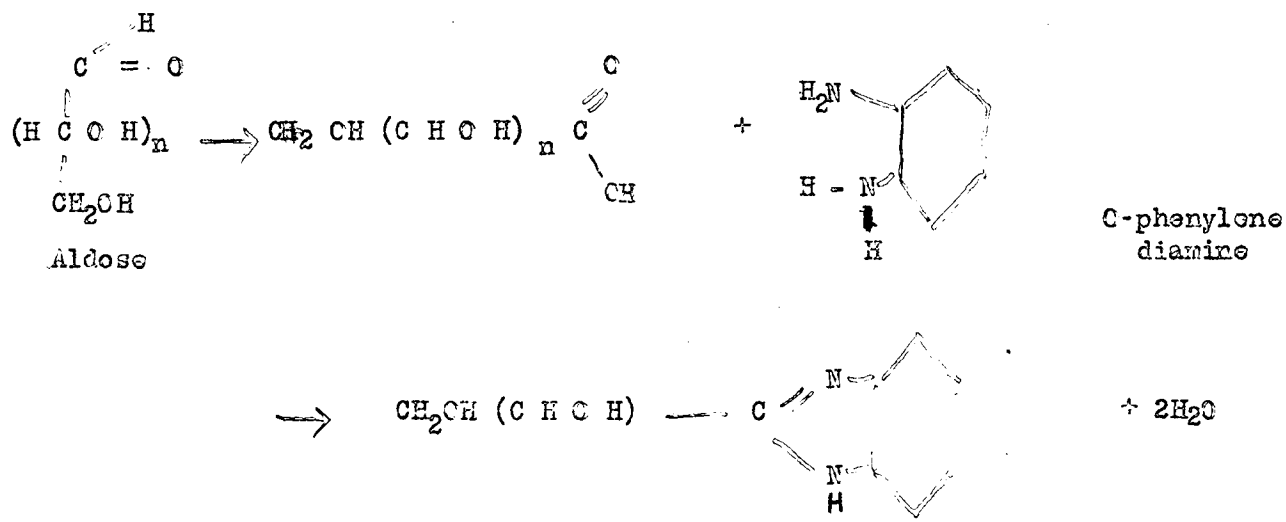
Ba salts of aldonic acids

condense with o-phenylene diamine
HCL + H_3PO_4 135°C.

Benzimidazoles
from mannose
rhamnose
lyxose

| HCl | $ZnCl_2$ 180°C

benzimidazole
from xylose.



Aldose

C-phenylene diamine

benzimidazole

Three oxidations were carried out on the mixed aldoses and the following results are typical:

2 g. aldose material used.

Wt. potassium salts 1.7g.

% potassium 15%

Wt. barium salts 1.45g.

% Barium 31%

The following crude barium and potassium salts were isolated by Moore and Link using pure sugars.

Crude Ba salts	% Ba
d lyxonic	37.9
d mannonic	35.7
l rhamnonic	39.3
d xylonic	39.6

Unpurified potassium salts	%K calculated	found
l arabonic	19.1	20.3
d galactonic	16.7	16.9
d gluconic	16.7	16.8

Attempts to condense o - phenylene diamine with the aldonic acids to give the benzimidazole derivatives were unsuccessful.

Mercaptalation experiments:

Wolfrom and co-workers used ethyl mercaptan to isolate diethyl mercaptal derivatives of the intermediates in the hydrolysis of cellulose to glucose with strong hydrocllloric acid[8,9,10,11].

Several attempts were made to apply their technique to a purified and concentrated syrup containing simple sugars from a cook on wood under

the conditions $\frac{A1/140/30/1}{7:1}$

No success was achieved.

Other methods of analysis which were considered were:-

Separation of sugars by chromatographic adsorbtion of their azoyl derivatives (p phenyl azo benzoyl derivatives).[12, 13, 14]

Analytical Separation of various classes of sugars by indirect methylation[15]

Distillation of propionyl derivatives[16]

Selective fermentation[2]

Specific analyses for xylose mannose and galactose (or galacturonic acid) on wood A2.

A large amount of wood A2 was extracted with hot water by adding 25 g. of wood to 3750 mls. of boiling water in 4 litre Erlenmeyer flask.

The water was brought to boiling point and placed in a boiling-water bath for one hour. The wood was then washed thoroughly by decantation and then filtered and air dried.

Estimation of Mannose.

The following method given by Wise[19] was used.

30.31 g. water extracted wood (O.D. basis) was boiled with 300 ml. 5% H Cl. for 3.5 hours. The contents of the hydrolysis flask are then filtered and the residue washed with 300 ml. of hot water. The combined filtrate and washings are neutralized with sodium hydroxide, made just acid with acetic acid, concentrated to 25 ml., filtered and diluted with water to 50 ml. This solution is then treated with 2.5-4 ml. phenylhydrazine and up to 5.0 ml. of

50 per cent. acetic acid. After standing for six hours the precipitated mannose phenylhydrazone is filtered, washed with water, alcohol, and ether, dried and weighed.

The weight of mannose phenylhydrazone times the factor 0.6 equals the weight of mannan.

The melting point of the phenylohdrazone was 188°C. in agreement with the M. P given by Butler and Crechter(20) for d mannose phenylhydrazone prepared by a similar method.

Wt water extracted C D wood A2		30.31 g.
Wt mannan		.121 g.
% mannan		.4%

GALACTAN.

The results here given are calculated as galactan, but it is not known whether the sugar unit is galactan or galacturonic acid in the original wood.

The method of estimation depends on the oxidation of galactan to mucic acid by nitric acid and is described by Wise.(19)

Wt water extracted O.D. wood A2		8.96 g.
Wt mucic acid	(a)	.086 g.
	(b)	.089 g.

wt galactan = .0875 X 1.2

= 1.17% galactan

The melting point of this mucic acid was 216°. The MP of mucic acid obtained from galactose and determined under similar conditions was 214°. Beilstein states that the melting point varies with rate of heating, but is 213-4° for a moderate rate of heating.

That the galactan units are present in the hemicellulose portion of the wood is indicated by the following experiment.

30 g. water extracted wood A2 moisture 10.74% was hydrolysed in the percolator without the inner tube (Fig 2) under the following conditions -

140°C for 180 minutes, 1% acid being passed through at the rate of 200 ml. per hour. Half of the hydrolysate so obtained was neutralised with barium carbonate and made slightly alkaline with barium hydroxide. After filtering, $4\frac{1}{2}$ g. nitric acid was added to the solution and it was evaporated on a water bath to 100 ml, filtered and evaporated again to 10 ml. Then - 50 ml 25% nitric acid was added and the procedure was completed according to the method of Wise.

Wt mucic acid . 140 g. MP. 215°D.

= .168 g. galactan

= 1.25% on O.D. wood.

An attempt to obtain mannose phenyl~~ohrazone~~ hydrazone from a similar hydrolysate was unsuccessful.

XYLAN.

Breddy and Jones[21] have developed a method for the estimation of xylose. It depends on the fact that xylose condenses with benzaldehyde dissolved in methanolic hydrogen chloride forming the sparingly soluble dibenzylidene dimethyl acetal of dxylose.

The weight of xylose can be obtained from the equation.

$$y = .482x + .055$$

where y = wt of xylose and x = wt of derivative. The method was first tried using .539 g of xylose which gave 1.009 g. of derivative which is the calculated weight. Its M.P was 210° the same as that given by Breddy and Jones for the pure substance.

Preparation of dibenzylidene dimethyl acetal of d xylose from a wood sugar solution obtained by percolation of water extracted wood A2 under the following conditions - 140°C for 180 minutes passing 1% acid at 200 mls. per hour. The solution contained 4.80 g. pentose in one litre as determined by furfural distillation and the bromination method estimation of the furfural. This

represented 16% of the weight of the original wood.

150 ml. of this solution was given after hydrolysis of 1½ hours, neutralized with sodium hydroxide, made just acid with sulphuric acid and evaporated to 75 mls. on a water bath.

The solution was then filtered and evaporated till as dry as possible underreduced pressure and the derivative was prepared in the usual way.

A weight of d. xylose dibenzylidene dimethyl acetal equal to .11 g. of xylose was obtained, whereas the original solution contained .72 xylose.

The melting point of the derivative was 208°C.

Some analyses of organic acids produced by dilute acid hydrolysis of e.obliqua in an autoclave of e. obliqua under varying conditions of temperature and time.

EXPERIMENTAL.

The hydrolyses were carried out in a small autoclave of acid resistant bronze by the method of Ralph and Wardrop(4). Woods A1 and A2 of -14 mesh B.S. particle size were hydrolysed with 1% H_2SO_4 using an acid : wood ratio of 7:1.

The sawdust charge was placed in the autoclave and thoroughly mixed with the required amount of acid of the desired concentration. The strength of the acid used was carefully checked by titration. The lid of the autoclave was secured and with the blow-off valve open, the vessel was lowered into an oil bath at somewhat above the desired temperature of reaction. The set temperature was generally attained in eleven to fifteen minutes and when all air had been displaced from the autoclave as indicated by the steady issue of steam, the valve was closed. Time was measured from the instant at which the desired temperature was reached. The reaction was terminated by immersing the autoclave in a cold water bath. Atmospheric pressure was reached in one to three minutes.

Reducing sugars, total organic acids and furfural were estimated by the methods previously described in this work.

Formic acid was estimated by its reduction of $HgCl_2$ to HgCl as described by the A.O.A.C.(22).

Acetic acid as estimated by subtracting formic acid from steam distillable acids. Justification for this procedure is given below.

Steam distillable acids were estimated by steaming a hydrolyate till the distillate was neutral to litmus paper.

The results are given in Tables III and IV. All results are percentages of the original wood.

TABLE III.

Effect of Temperature on Acid Production.

Wood A1

	A1/200/30/1 7:1	A1/175/30/1 7:1	A1/140/30/1 7:1
Total Acid #	21.0	6.6	4.5
Steam distillable acids #	12.3	4.8	2.8
Formic Acid	5.9	.75	-
Acetic acid	6.4	4.0	2.8

TABLE IV.

Effect of time on Acid Production at 184°C.

Wood A2

	A2/184/30/1 7:1	A2/184/100/1 7:1	A2/184/240/1 7:1
Total loss	57.6	55.3	53.6
Reducing sugar as Glucose	21.2	3.6	0.0
Furfural	4.2	4.1	0.3
Total acid #	12.0	22.1	22.3
Steam distillable acids #		13.8	
Formic acid		7.4	
Acetic acid		6.4	

Calculated as acetic acid.

DISCUSSION:

Table III indicates the effect of temperature on the nature of the acids formed. At low temperatures no formic acid is present and it is probable that acetic acid only arises from acetyl groups associated with cellulose (2,5,6). As the temperature increases increasing amounts of formic and acetic acids are obtained from the breakdown of reducing sugars.

Table IV indicates the effect of time on the breakdown of reducing sugars which have been formed by hydrolysis but it is to be noted that there is not a proprotional increase in yield of organic acids.

EXPERIMENTAL:

The sodium salts of the steam distilled acids from a cook $\frac{A2/184/100/1}{7:1}$ were distilled with dilute sulphuric acid and the distillate treated with $FeCl_3$. If the colouration formed is soluble in amyl alcohol propionic acid is indicated but this was not the case.

The solium salts of steam distillable acids from another cook under the conditions $\frac{A2/184/100/1}{7:1}$ were evaporated to dryness and then heated with concentrated sulphuric acid until formic acid was destroyed as indicated by the fact that no more bubbles of carbon monoxide were evolved. The solution was diluted to 20% sulphuric acid and the volatile acids were distilled off. The distillate was exactly neutralised with barium hydroxide and a little barium sulphate was filtered off. The solution was then evaporated to dryness on a water bath and dried in an air oven at 105°C. According to Beilstein barium acetate loses its last molecule of hydration at 41°C. A barium estimation on the molecular weight gave 59.64 of acetic acid (60.05).

The residue after steam distillation was concentrated and extracted with other. The other was evaporated and the residue treated with Ig & Na_2CO_3 to test for levulinic acid but no iodoform was detected.

DISCUSSION:

It is concluded from these experiments that only formic and acetic acids are present in the steam distillable portion.

That levulinic acid was not detected in the residue is surprising since Thomas and Schuette[23] prepared levulinic acid by the action of dilute hydrochloric on starch at 162°C. for five hours.

The presence of tannic acids also has to be considered. It is unlikely that uronic acids would be present since they are easily decomposed by hot dilute acid to furfural and carbon-dioxide.

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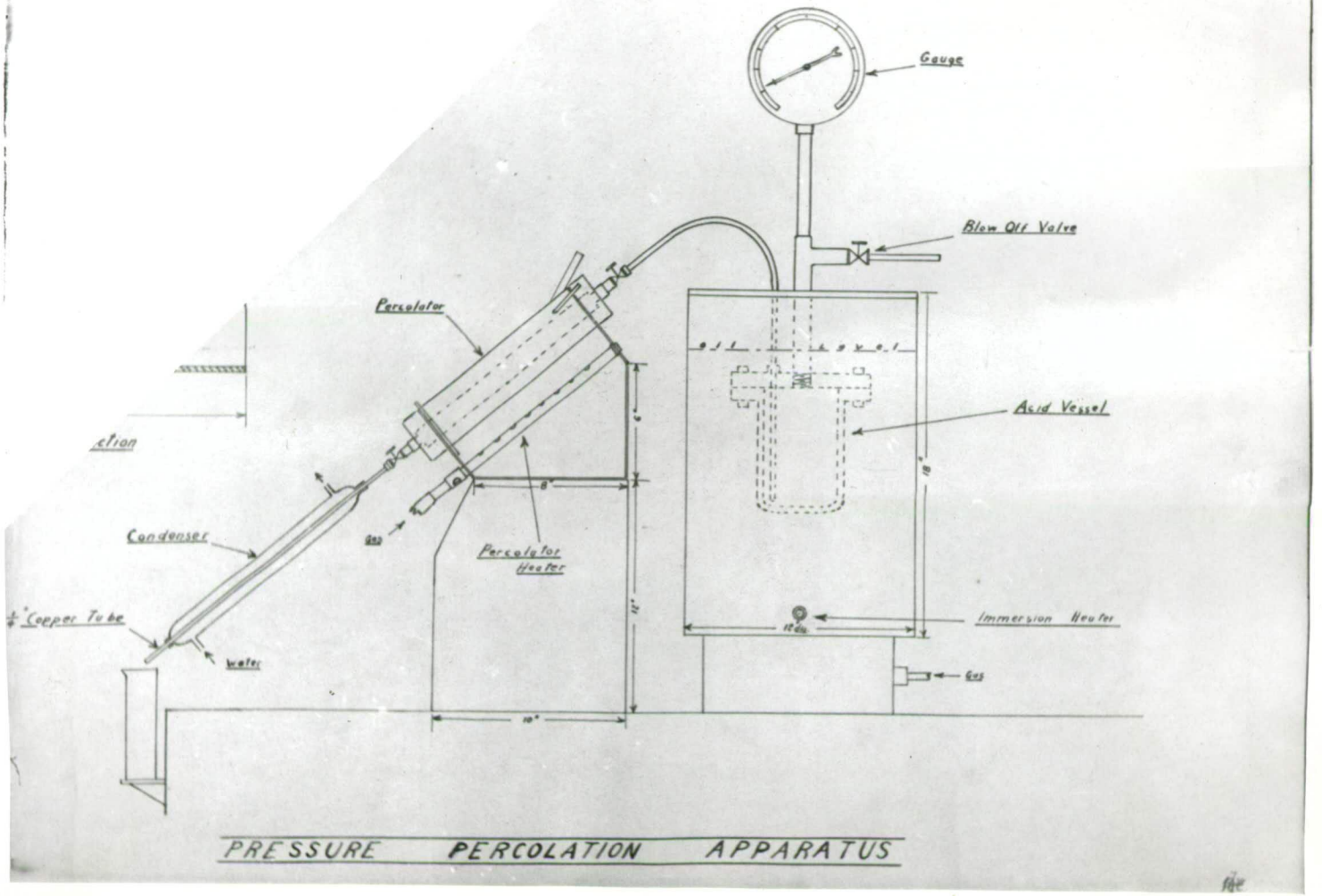
Gauge
Blow Off Valve
Percolator
Acid Vessel
Condenser
Gas
Percolator Heater
Immersion Heater
Gas
water
PRESSURE PERCOLATION APPARATUS

Figure 1.

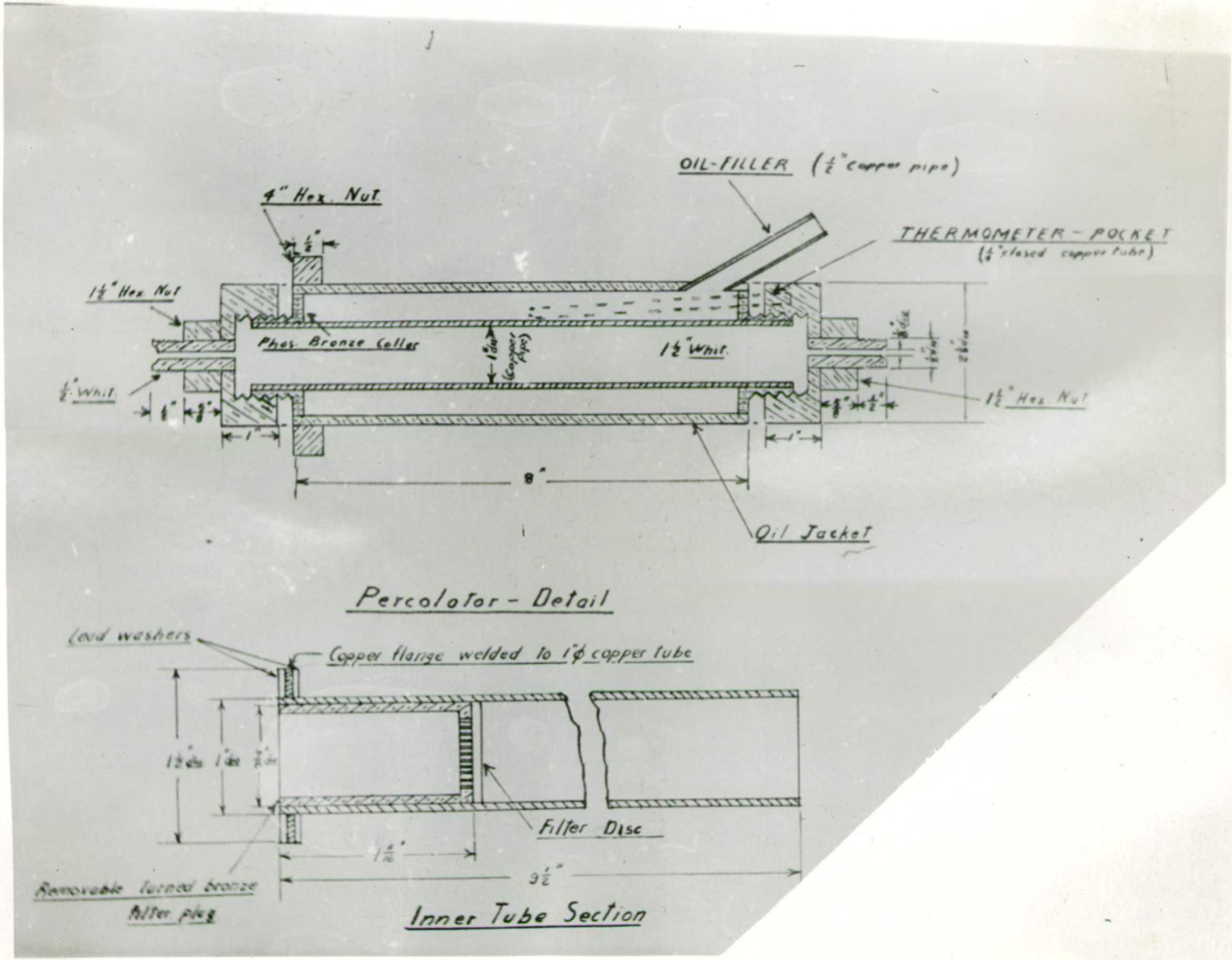
OIL-FILLER (½" copper pipe)
4" Hex. Nut
THERMOMETER-POCKET
(½" closed copper tube)
1½" Hex Nut
Phos. Bronze Collar
1½" Whit.
½" Whit.
1½" Hex Nut
8"
Oil Jacket
Percolator - Detail
Lead washers
Copper flange welded to 1" ϕ copper tube
Filter Disc
Removable turned bronze
filter plug
Inner Tube Section

Figure 2.

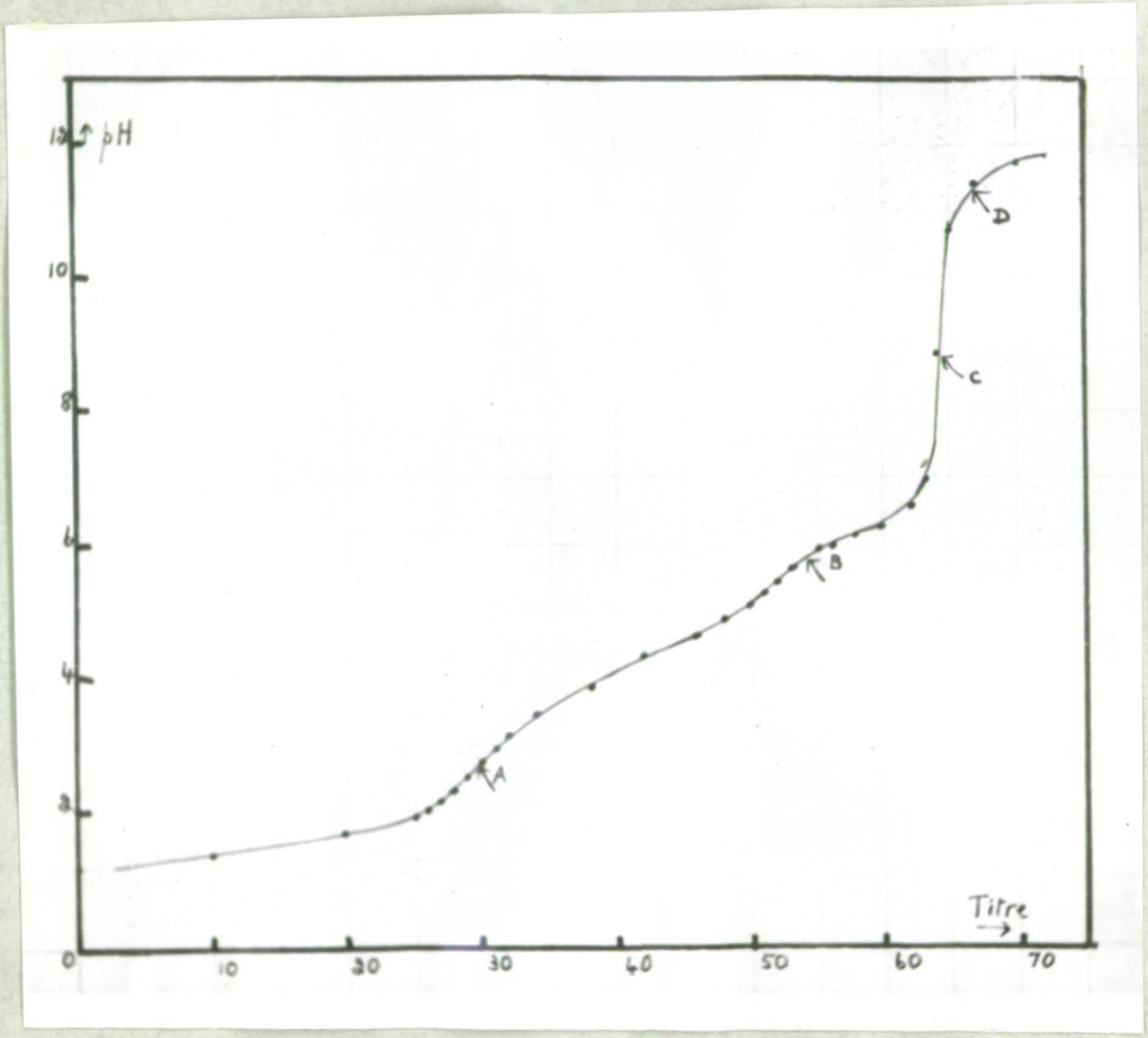

Figure 3.

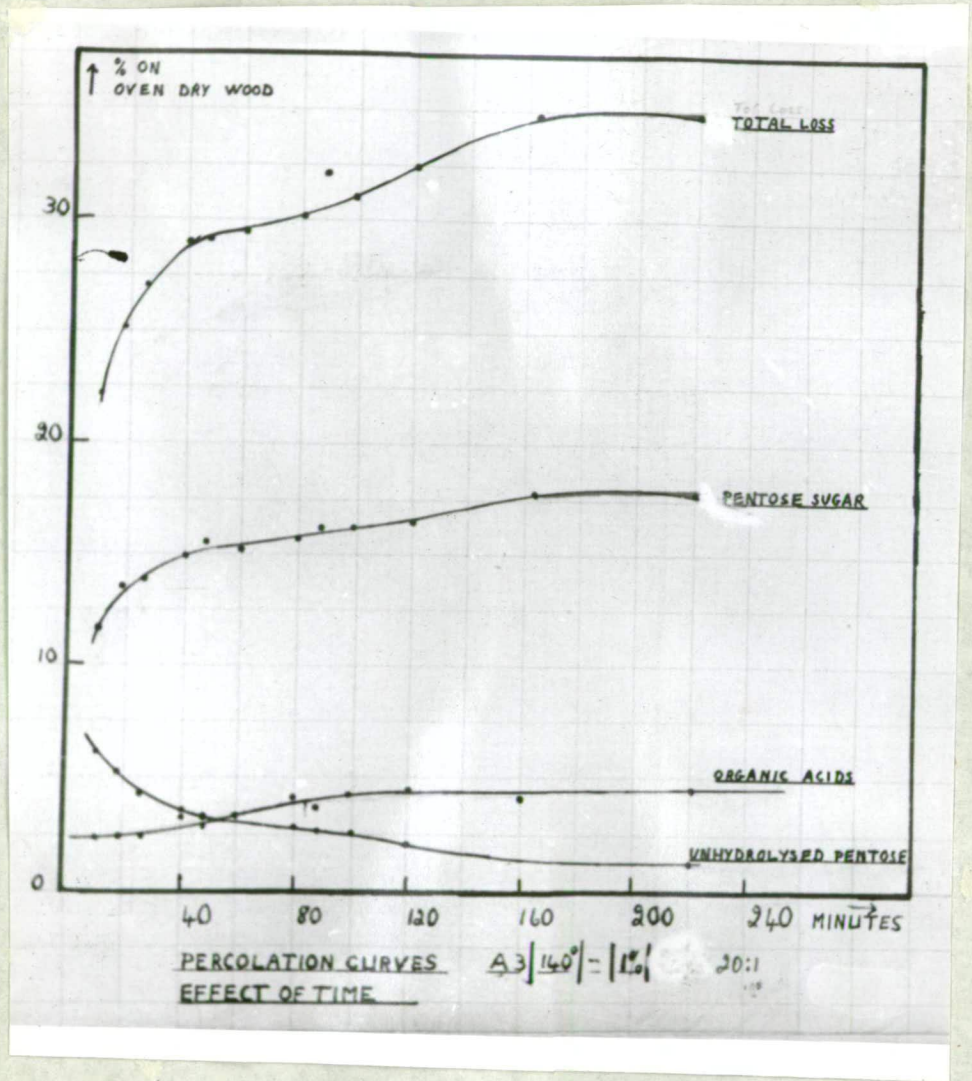
% ON
OVEN DRY WOOD
TOTAL LOSS
PENTOSE SUGAR
ORGANIC ACIDS
UNHYDROLYSED PENTOSE
30
20
10
0
40
80
120
160
200
240
MINUTES
PERCOLATION CURVES
EFFECT OF TIME
A3 | 140° | = | 1% |
20:1

Figure 4.

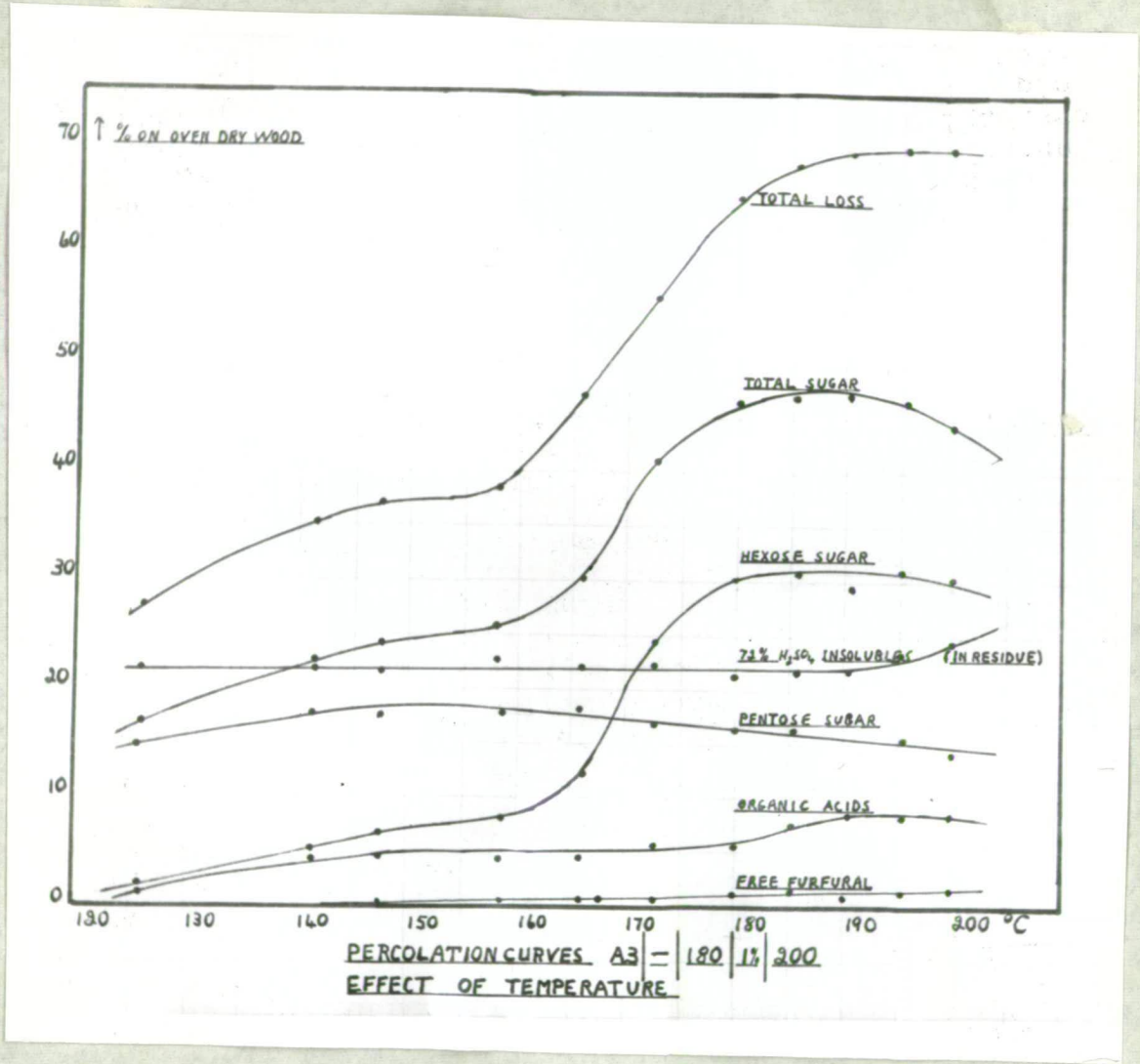
% ON OVEN DRY WOOD
TOTAL LOSS
TOTAL SUGAR
HEXOSE SUGAR
72% H2SO4 INSOLUBLES (IN RESIDUE)
PENTOSE SUGAR
ORGANIC ACIDS
FREE FURFURAL
70
60
50
40
30
20
10
0
130
130
140
150
160
170
180
190
200 °C
PERCOLATION CURVES A3 — 180 1% 200
EFFECT OF TEMPERATURE

Figure 5.

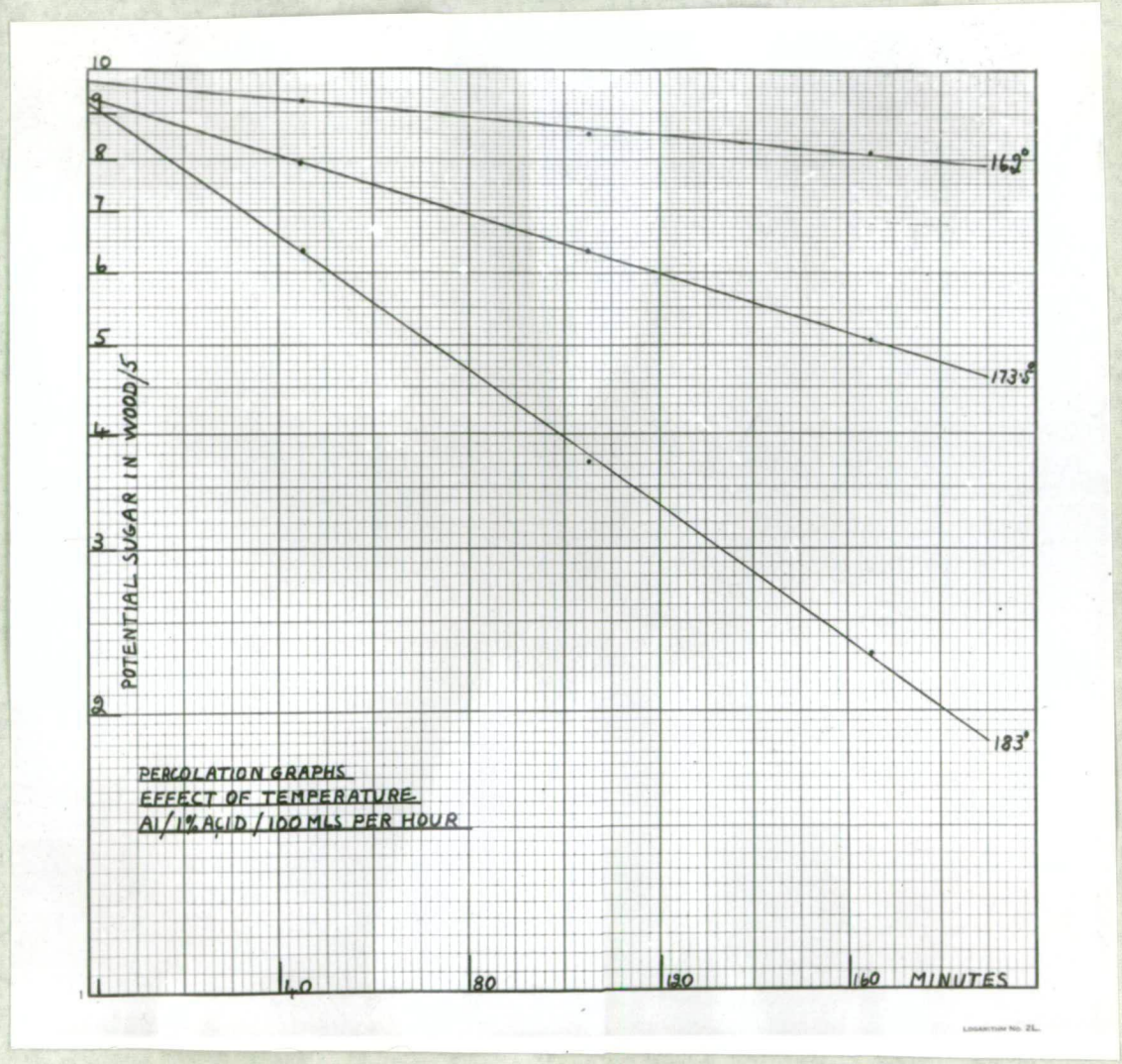
10
9
8
7
6
5
4
3
2
1
POTENTIAL SUGAR IN WOOD/5'
162°
173.5°
183°
PERCOLATION GRAPHS
EFFECT OF TEMPERATURE
AT 1% ACID / 100 MLS PER HOUR
40
80
120
160 MINUTES

Figure 6.

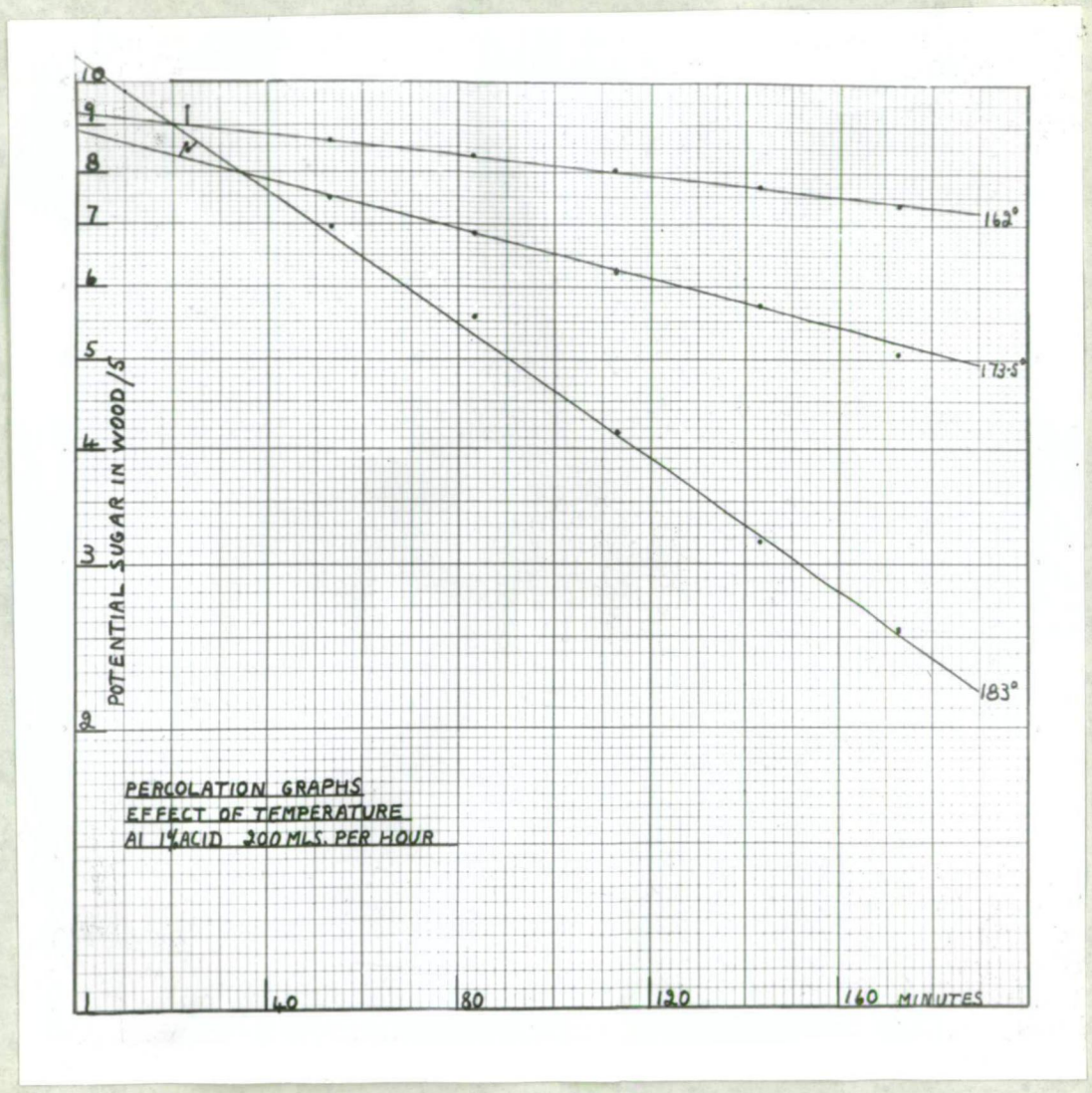
10
9
8
7
6
5
4
3
2
1
POTENTIAL SUGAR IN WOOD/S
162°
173·5°
183°
PERCOLATION GRAPHS
EFFECT OF TEMPERATURE
AT 1% ACID 200 MLS. PER HOUR
40
80
120
160 MINUTES

Figure 7.

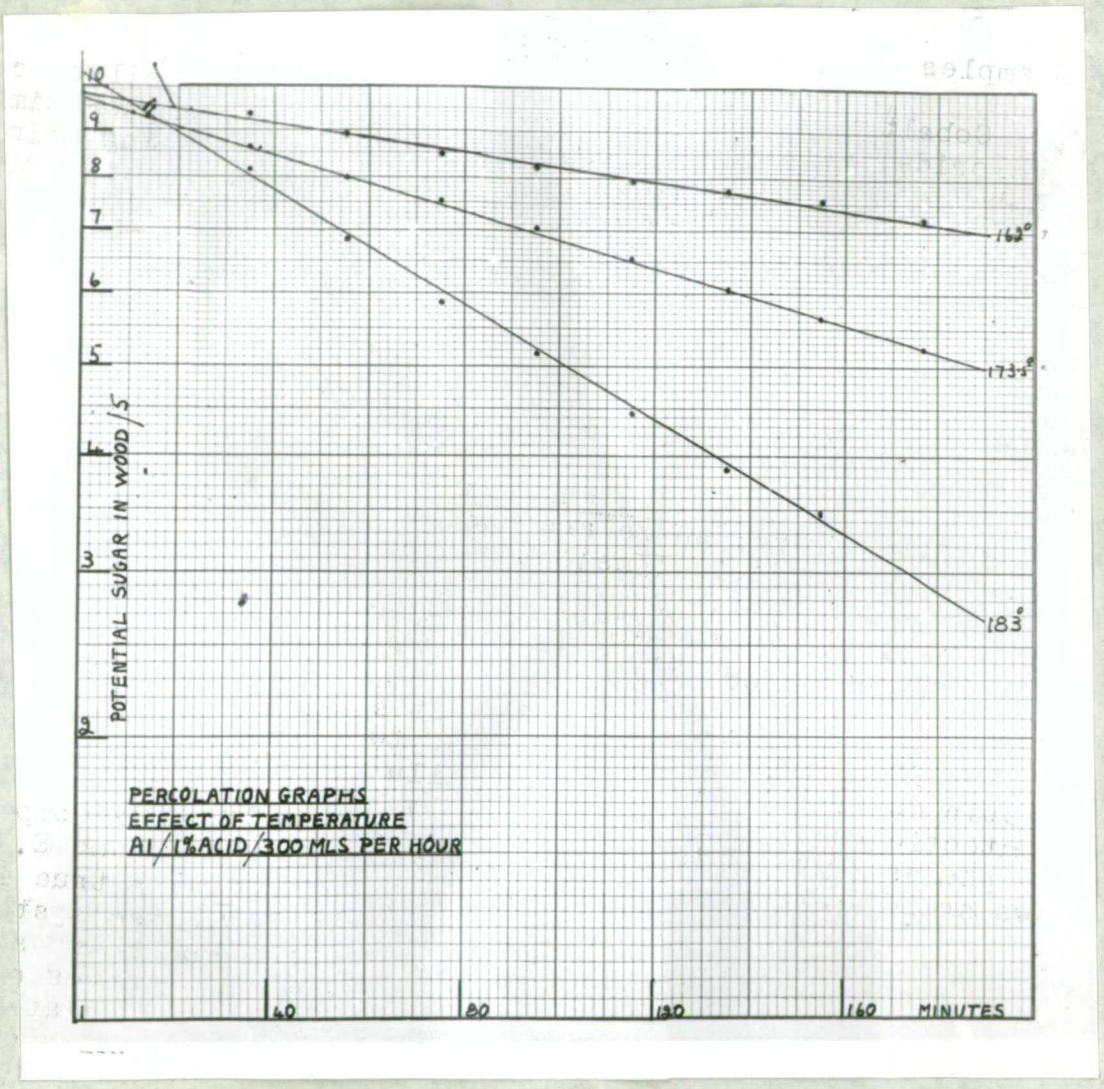
POTENTIAL SUGAR IN WOOD /5
10
9
8
7
6
5
4
3
2
1
40
80
120
160
MINUTES
169°
173·5°
183°
PERCOLATION GRAPHS
EFFECT OF TEMPERATURE
A1/1% ACID/300 MLS PER HOUR

Figure 8.

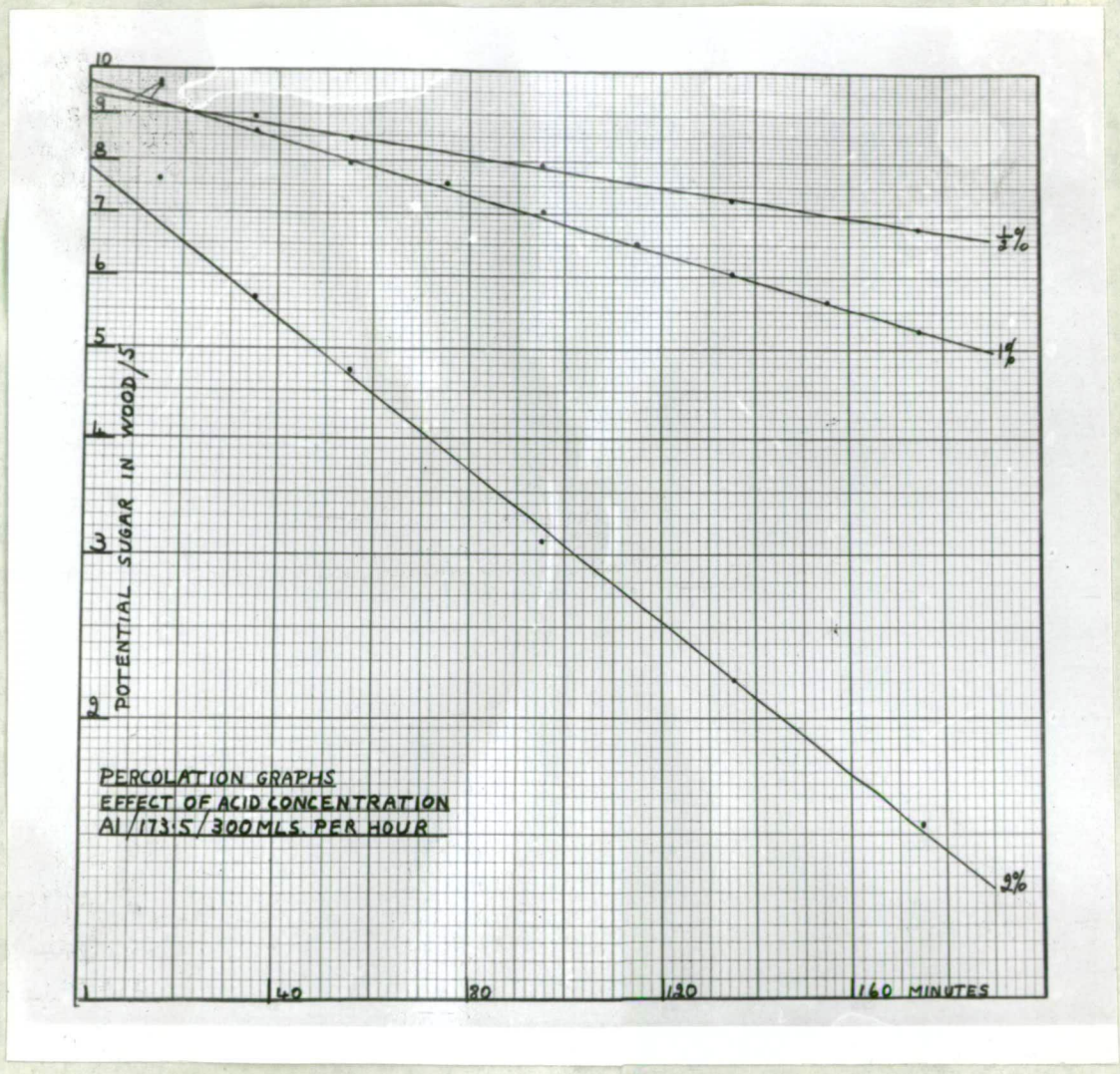
10
9
8
7
6
5
4
3
2
POTENTIAL SUGAR IN WOOD/S
PERCOLATION GRAPHS
EFFECT OF ACID CONCENTRATION
AI/173:S/300 MLS. PER HOUR
½%
1%
2%
1
40
80
120
160 MINUTES

Figure 9.

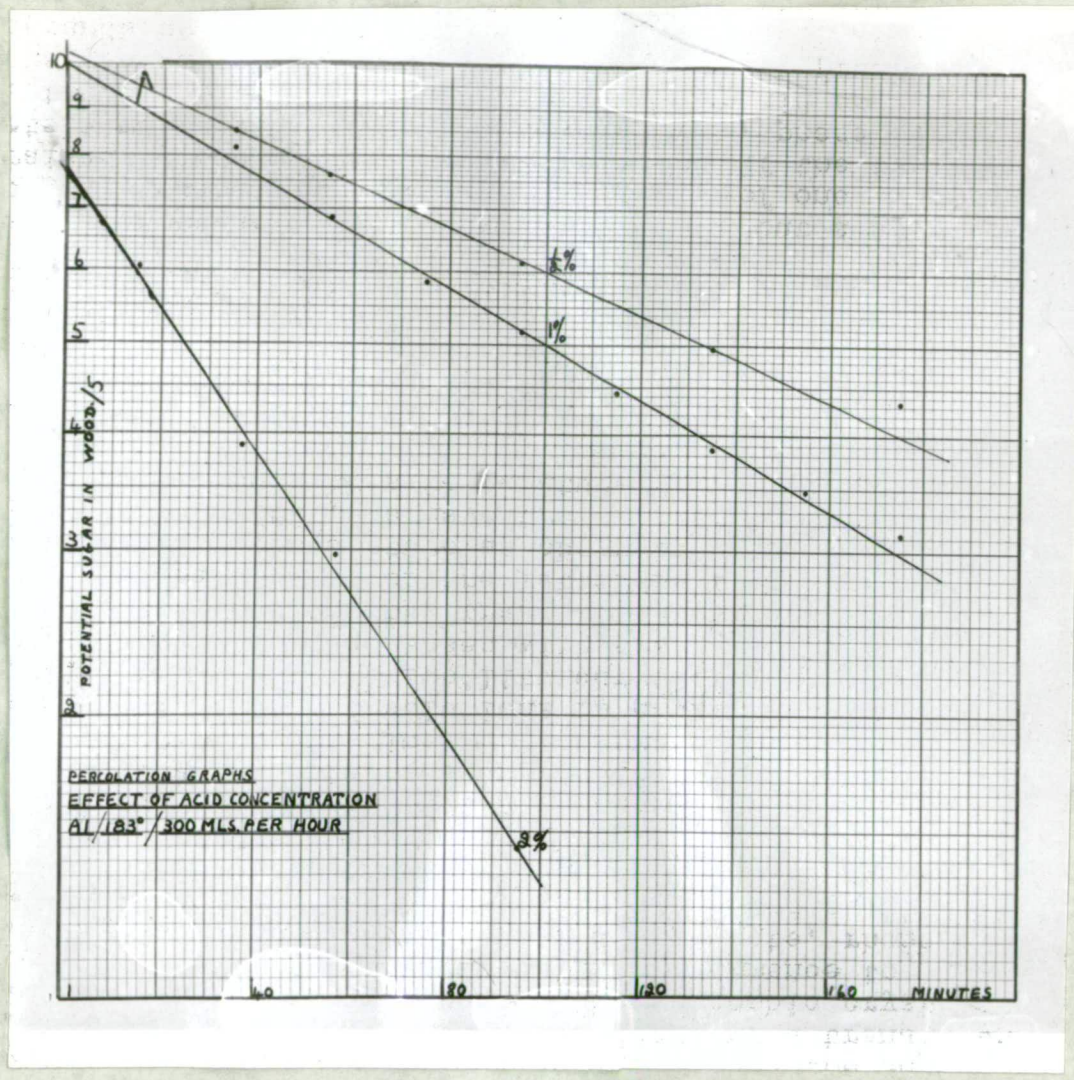
A
½%
1%
3%
POTENTIAL SUGAR IN WOOD/5
PERCOLATION GRAPHS
EFFECT OF ACID CONCENTRATION
AT 183° / 300 MLS. PER HOUR
40
80
120
160
MINUTES

Figure 10.

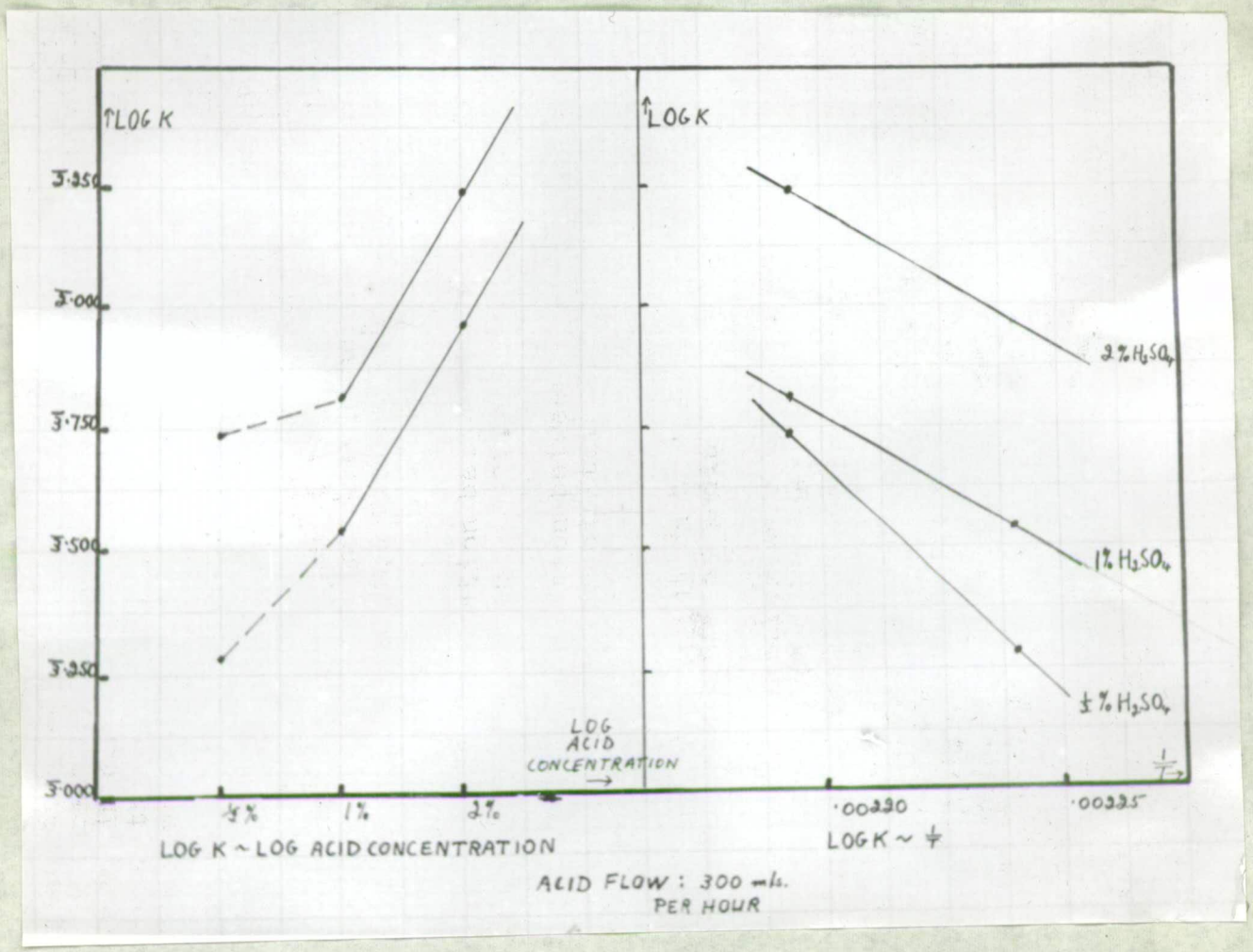
↑LOG K
3·250
3·000
3·750
3·500
3·250
3·000
½%
1%
2%
LOG ACID CONCENTRATION →
LOG K ~ LOG ACID CONCENTRATION
↑LOG K
2% H_2SO_4
1% H_2SO_4
½% H_2SO_4
·00220
·00225
$\frac{1}{T}$
LOG K ~ $\frac{1}{T}$
ACID FLOW : 300 ml. PER HOUR

Figure 11.

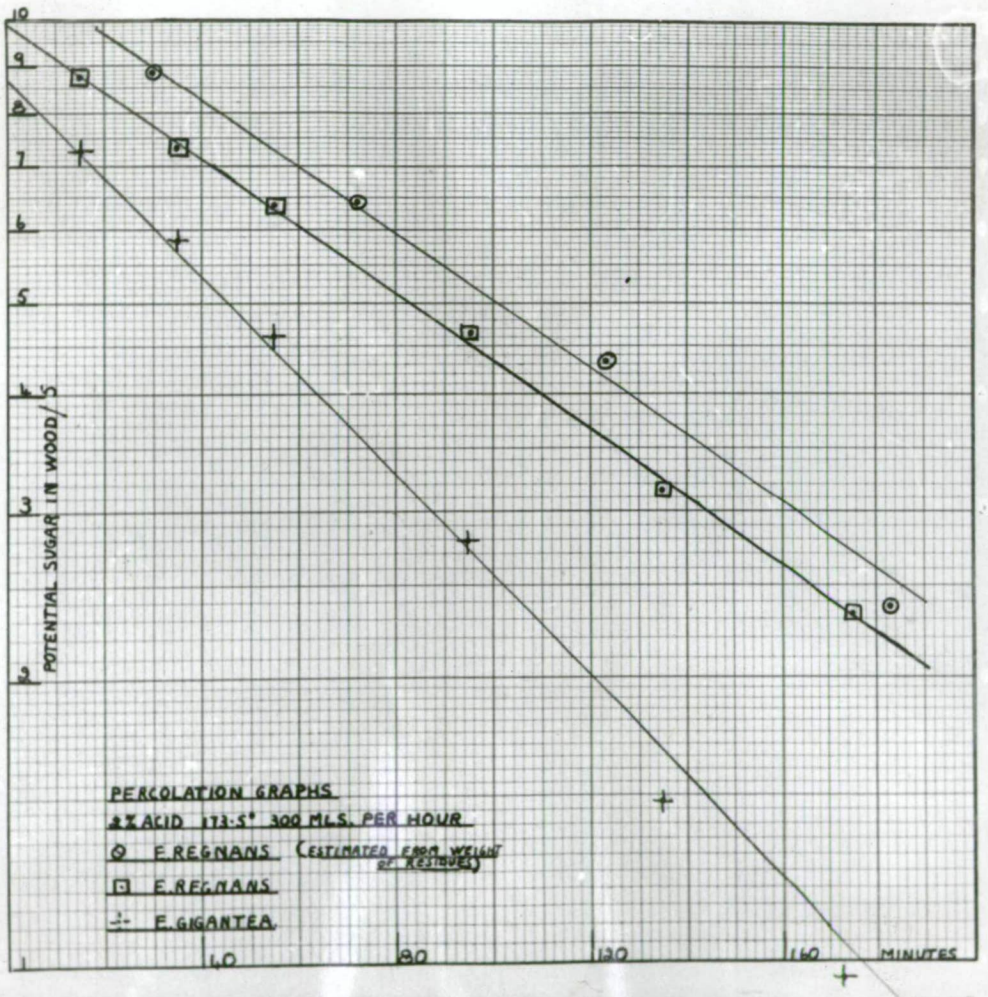
POTENTIAL SUGAR IN WOOD/
10
9
8
7
6
5
4·5
3
2
1
40
80
120
160
MINUTES
PERCOLATION GRAPHS
2% ACID 173·5° 300 M.L.S. PER HOUR
⊙ E. REGNANS (ESTIMATED FROM WEIGHT OF RESIDUE)
⊡ E. REGNANS
+ E. GIGANTEA

Figure 12.

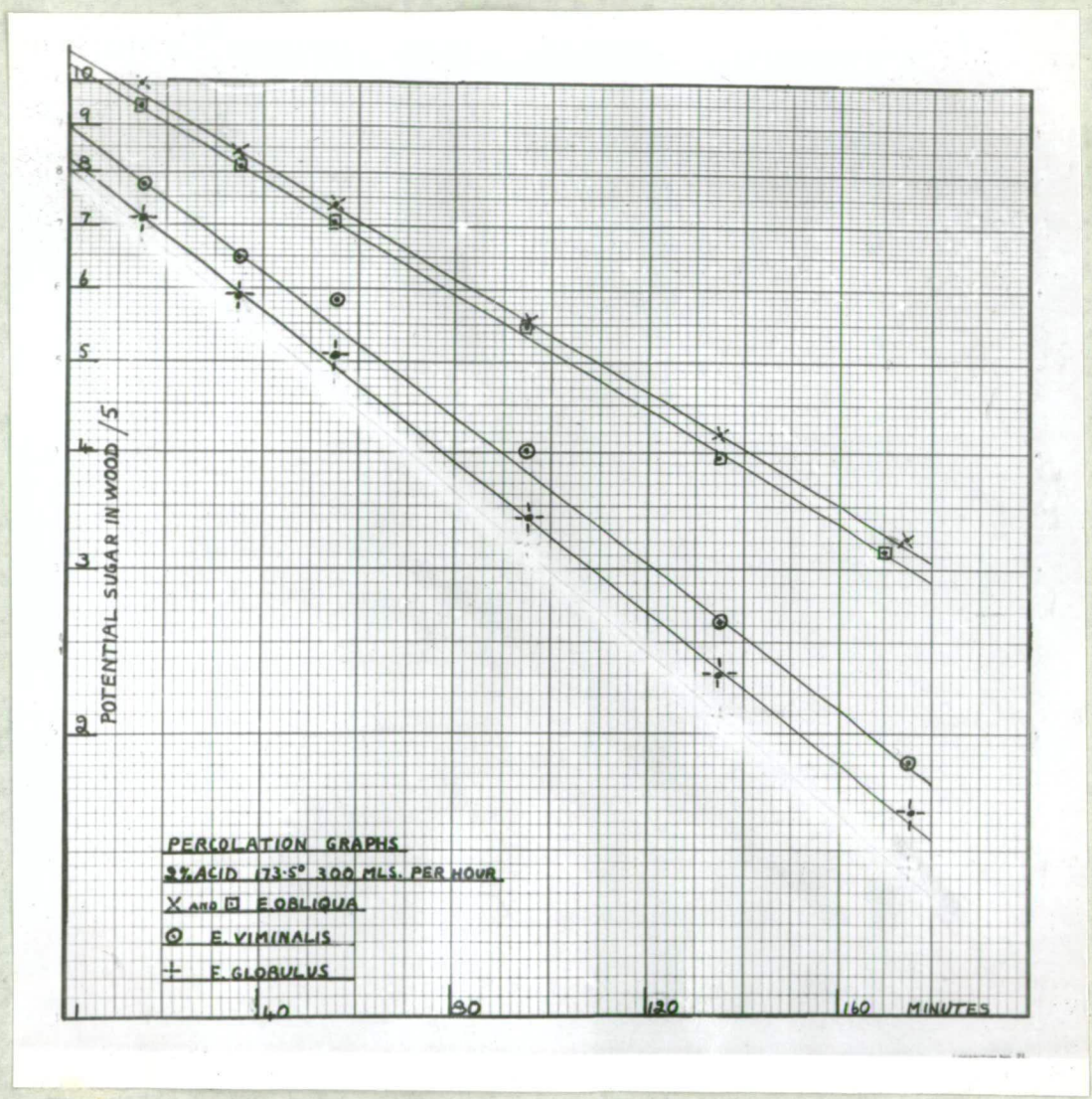
POTENTIAL SUGAR IN WOOD /5
10
9
8
7
6
5
4
3
2
1
PERCOLATION GRAPHS
2% ACID 173·5° 300 MLS. PER HOUR.
X AND ⊡ E. OBLIQUA
⊙ E. VIMINALIS
+ E. GLOBULUS
40
80
120
160
MINUTES

Figure 13.

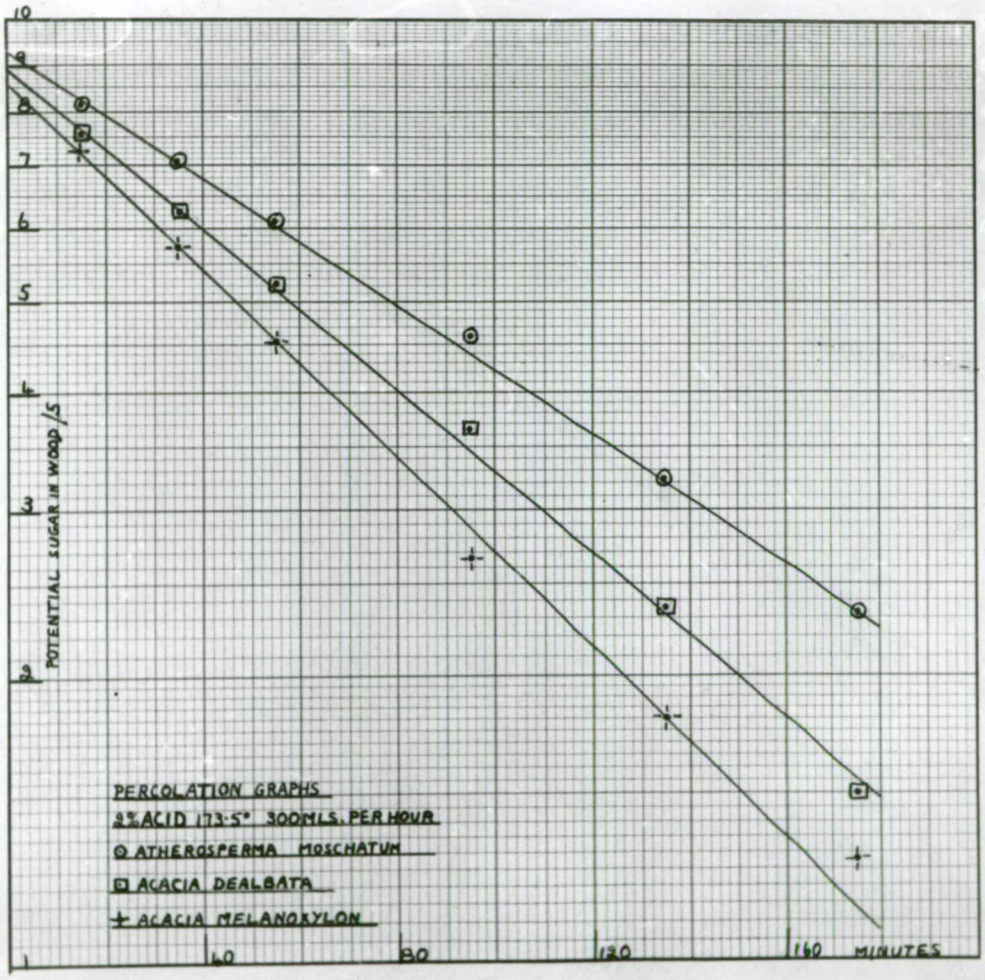
POTENTIAL SUGAR IN WOOD /S
10
9
8
7
6
5
4
3
2
1
40
80
120
160
MINUTES
PERCOLATION GRAPHS
2% ACID 173·5° 300 MLS. PER HOUR
⊙ ATHEROSPERMA MOSCHATUM
⊡ ACACIA DEALBATA
+ ACACIA MELANOXYLON

Figure 14.

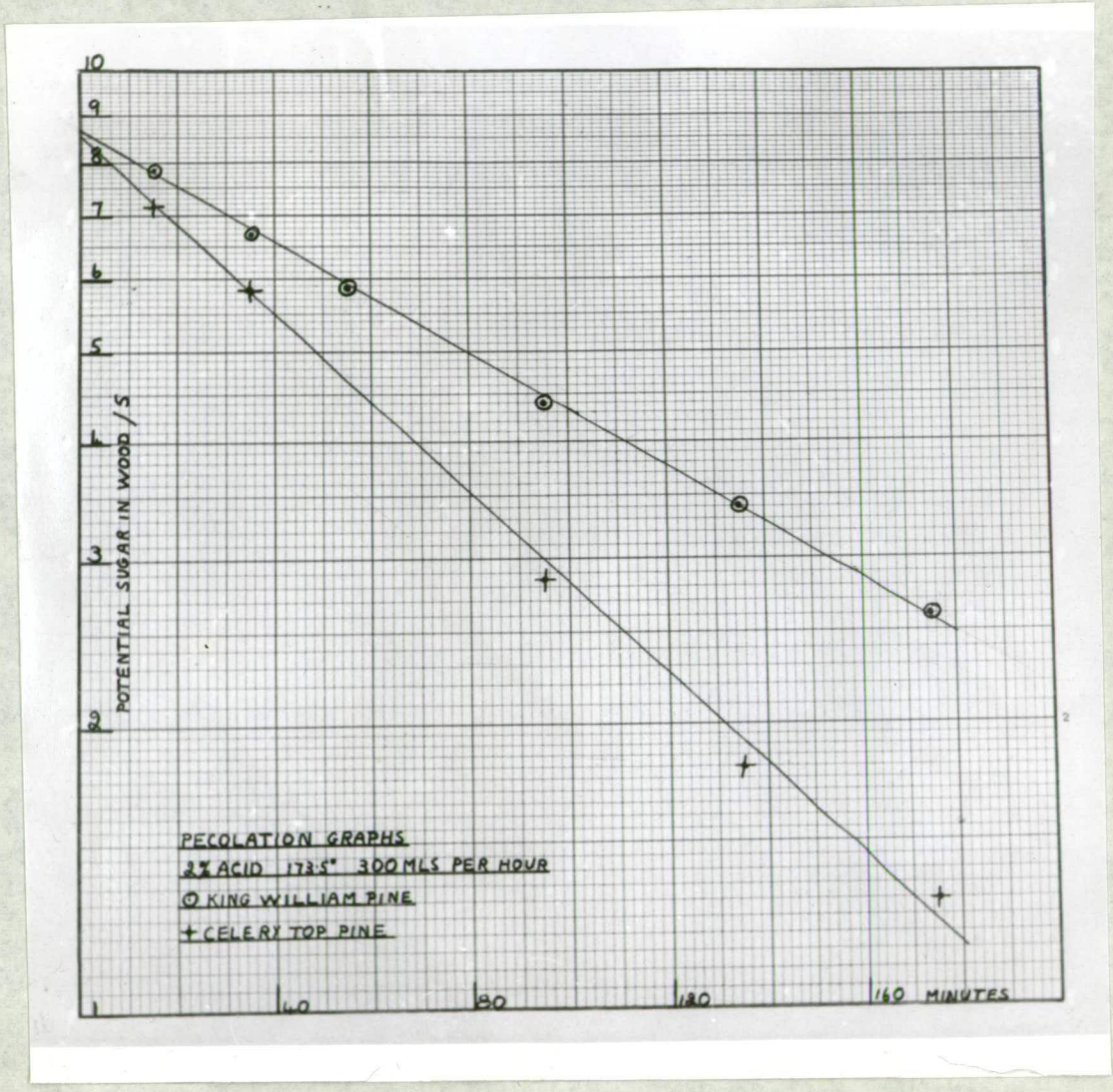
10
9
8
7
6
5
4
3
2
1
POTENTIAL SUGAR IN WOOD /S
PECOLATION GRAPHS
2% ACID 173·5° 300 MLS PER HOUR
⊙ KING WILLIAM PINE
+ CELERY TOP PINE
40
80
120
160 MINUTES

Figure 15.

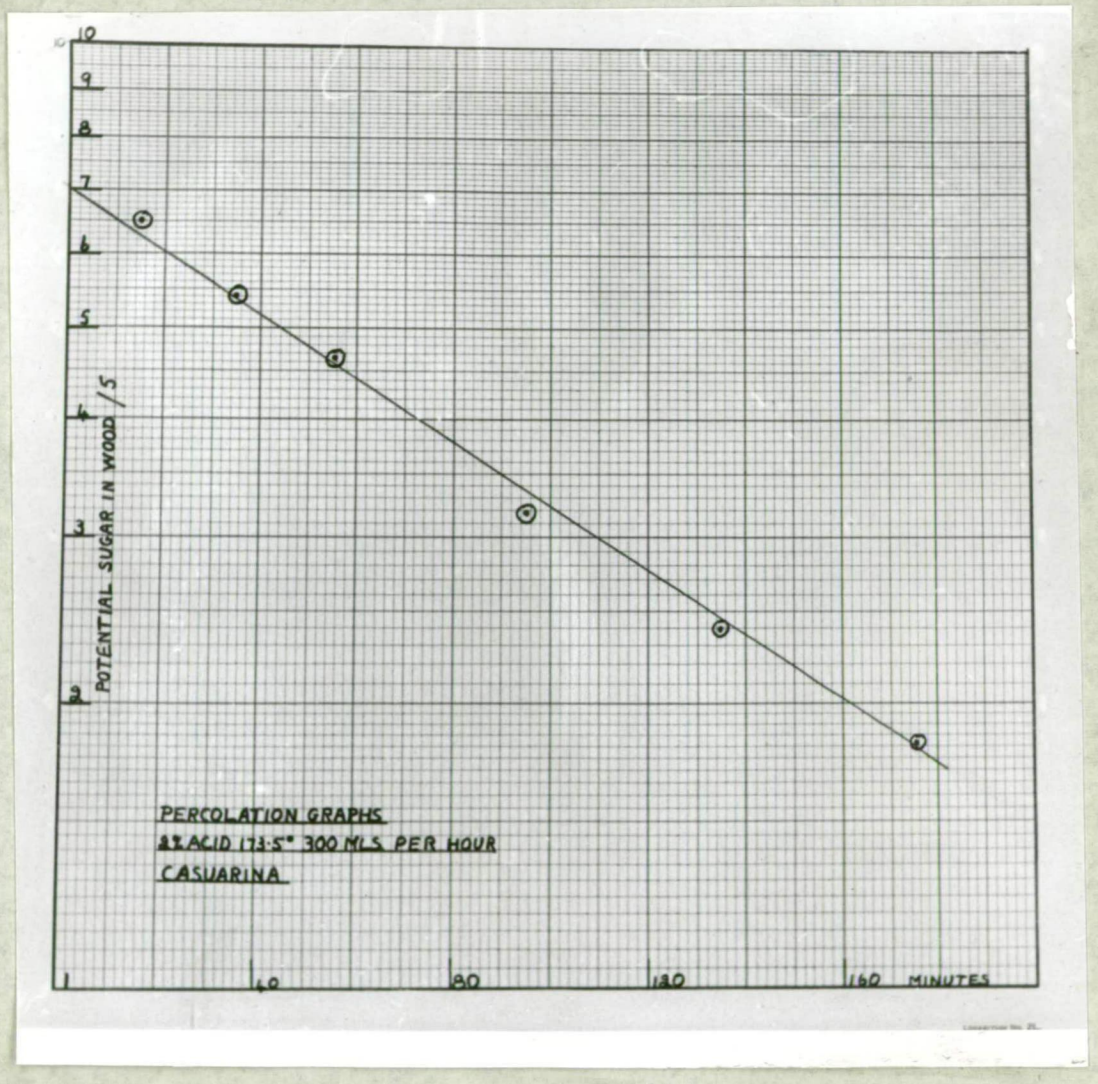
10
9
8
7
6
5
4
3
2
POTENTIAL SUGAR IN WOOD /5
PERCOLATION GRAPHS
2% ACID 173·5° 300 MLS PER HOUR
CASUARINA
1
40
80
120
160
MINUTES

Figure 16.